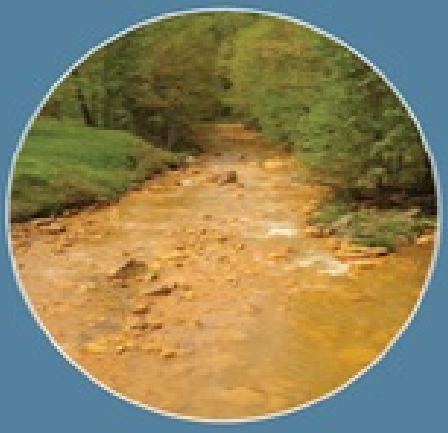
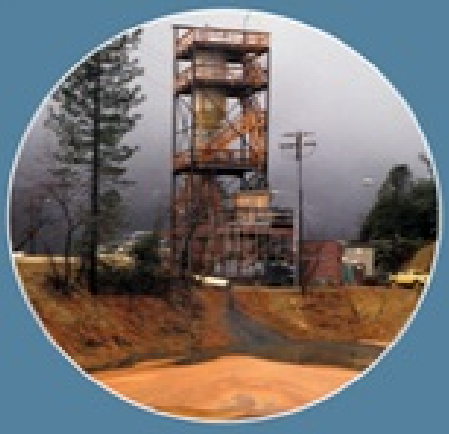


Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils

Causes, Assessment, Prediction, Prevention, and Remediation



JAMES A. JACOBS
JAY H. LEHR
STEPHEN M. TESTA

WILEY

ACID MINE DRAINAGE, ROCK DRAINAGE, AND ACID SULFATE SOILS

Causes, Assessment, Prediction, Prevention, and Remediation

Edited by

JAMES A. JACOBS
JAY H. LEHR
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PREFACE

Acid drainage is a widespread universal biogeochemical process that has existed on Earth for eons, producing acidic waters rich in sulfuric acid and toxic metals, as well as potential resources. Acid drainage occurs at coal mines and is associated with hardrock metal ore deposits, road or building development projects, naturally occurring gossans, or with coastal marine sediments producing acid sulfate soils. Its presence reflects the complex biogeochemical interaction of an oxidizing agent, typically oxygen, which reacts with iron sulfide compounds catalyzed by iron- or sulfur-oxidizing microbial organisms, primarily bacteria in the presence of water. Most commonly, pyrite is exposed at the surface through natural processes or a development project, and the oxidation of the iron sulfide compound begins to dissolve, creating the exothermic reactions and by-products described in these pages. This book is a compilation or status report on what is known on the subject of acid drainage, sometimes described in the literature under the topics of acid mine drainage, acid rock drainage, and acid sulfate soils.

Acid drainage occurs in many environments, as discussed in Part I, Causes of Acid Mine Drainage, Rock Drainage, and Sulfate Soils, which focuses on the biogeochemistry of acid mine drainage, rock drainage, and sulfate soils. The telltale dark red to orange river water and sediments are found worldwide in a variety of environmental settings, all associated with sulfide oxidation. Primarily microbially induced, the acid drainage process produces sulfuric acid, creating low-pH conditions in creeks, streams, rivers, and associated water basins.

Acid drainage relating to stream characterization, aquatic and biological sampling, evaluation of aquatic resources, and unusual aspects of sulfide oxidation are discussed in Part II, Assessment of Acid Mine Drainage, Rock Drainage, and Sulfate Soils. As part of the acid drainage process, other toxic metals become solubilized by the acidic waters, which have been documented to harm aquatic organisms. Large fish kills, up to severe degradation of surface water and groundwater resources, have been well documented in the literature in areas containing acid drainage.

In Part III, Prediction and Prevention of Acid Drainage, we address just how far we have come in predicting acid drainage accurately. The prediction of acid drainage has been challenging. Based on the shallow exposure of copper, gold, silver, and other metal ores, we know that mining in the Rio Tinto area of Spain dates back over 5000 years. Those ores contain iron sulfides that oxidize during mining disturbance when exposed to the oxygen in the atmosphere. Unfortunately, once the process of acid drainage starts, it is virtually impossible to stop the biogeochemical reactions. Various predictive tools and methods, including acid–base accounting, kinetic testing, block modeling, petrology, and mineralogy studies, are described in Part III. Policy, regulation, and brownfield redevelopment are also discussed.

Various passive and active cleanup methods to treat acid drainage once the biogeochemical process begins are described in Part IV, Remediation of Acid Drainage, Rock Drainage, and Sulfate Soils. Reusing the wastes from acid drainage is the best method for sustainable mining and development. Acid drainage and the biogeochemical processes involved can be enhanced and used for resource recovery. In Part V we provide a variety of useful reference appendixes.

We also address several general questions that provide an overview and fundamental understanding of acid drainage:

- Are all sulfur oxidation reactions aboveground?

Not all sulfur oxidation reactions are aboveground. Sulfur oxidation reactions occur in some unlikely

places in the subsurface. Understanding water geochemistry and changes in redox conditions is important for water managers who are monitoring and using aquifer recharge systems. Population growth combined with global climate changes requires more astute use and optimization of subsurface aquifers for large-scale water storage systems. In these cases, oxygen-rich surface or treated water can be pumped into subsurface aquifers for storage and reuse. The contact chemistry of injecting highly oxygenated surface or treated waters into reduced pyrite-rich aquifers causes the same acid drainage reactions in the subsurface, frequently liberating arsenic through the production of sulfuric acid and dissolution of the pyrite grains. Examples of aquifer storage and sulfide oxidation, and arsenic mobilization issues from southern Florida are discussed.

- Can acid drainage be a resource?

Acid mine drainage resources such as the various forms of vitriol have been known for millennia. The ubiquitous bright yellow staining found in rivers and creeks as a result of naturally occurring sulfur oxidation was undoubtedly noted by prehistoric man. The Rio Tinto acid mine drainage area in southern Spain presents an example of a long-term, ongoing environmental challenge with enormous resource potential. Even miners working around 3000 B.C. and later alchemists were aware of the magical and reactive characteristics of the acidic waters of the Rio Tinto. Rio Tinto, the “red river,” was named for the dark reddish orange mine drainage that empties into the waterway. For about 5000 years, the acid drainage from Rio Tinto, rich in sulfuric acid and metals, was used as a resource by the many civilizations that controlled the mines. Called “oil of vitriol” by medieval European alchemists, this chemical was used for tanning leather and dying cloth. The acid mine drainage chemicals were also used in early medicines, especially for treating the eyes. Although associated as a waste product with acid drainage, sulfuric acid is still greatly valued and produced synthetically in chemical plants. Sulfuric acid is currently one of the world's largest-volume industrial chemicals and is used in numerous manufacturing processes.

Today, bioleaching or biomining methods use changes in redox conditions to mobilize metal cations from insoluble ores by biological oxidation and complexation processes. An important bacterium of acid mine drainage which is also used in the bioleaching mining process is *Acidithiobacillus ferrooxidans*, which oxidizes ferrous iron (Fe^{2+}) and generates ferric iron (Fe^{3+}), an oxidant. This microbe, common to acid mine drainage environments, is used in the bioleaching process to leach copper from low-grade mine tailings and waste mining rock. DNA studies indicate a large list of iron- and sulfur-oxidizing bacteria and archaea capable of withstanding extremes in pH and temperature while obtaining energy from the iron and sulfur oxidation processes. The earlier scientific literature refers to iron- and sulfur-oxidizing bacteria, and the primary transformations described in this book are still performed by these microbes. However, more recently, microbiology researchers using detailed genetic testing techniques refer to richer, more complex, and more diverse acid mine drainage microbial communities. In one study, these communities contain microbial eukaryotes consisting of both fungi and protists that can create biofilm structures in the areas colonized by the microbial community. According to researchers, these biofilm structures can affect the abundance of both the more abundant aerobic bacteria and archaea and the microbial community composition through a variety of previously unknown interactions and complex mechanisms. Clearly, our understanding of the microbiology of acid mine drainage is evolving, which provides improvements in our resource recovery options. The optimization of the biogeochemical process in metal resource recovery has increased copper recovery rates and reduced the operating costs of mining companies using this enhanced mining method, called *bioleaching*. Future hardrock mining operations will require the expertise of multidisciplinary teams of mining engineers, mining geologists, geochemists, microbiologists, hydrogeologists, environmental specialists, wildlife biologists, and others to maximize

resource recovery while minimizing environmental degradation. Case studies provide examples of various treatment technologies. The cold-mix asphalt process can use mine tailings and mining wastes to create valuable recycled products to be used locally. The asphalt product prevents the metals from leaching and stops the acid generation process when used properly.

Shale gas fracturing, currently employed in Pennsylvania and several other states, requires millions of gallons of water per well. Recycling of acid mine drainage for hydraulic fracturing will divert some of the more than 300 million gallons of mine drainage water that flows into Pennsylvania's rivers and streams each day. Acid mine waters are also being considered a valuable resource in West Virginia, Pennsylvania, Maryland, and other states where treated and recycled water is used in aquaculture projects to grow striped bass, rainbow trout, char, yellow perch, and catfish. These recent projects demonstrate the value of some of the resources derived from acid drainage.

- How long has acid drainage occurred on Earth?

The sulfur oxidation reactions catalyzed by the iron- and sulfur-oxidizing microorganisms have been on the planet for eons, but they did not occur within the first few million years after formation of the planet, about 4.6 billion years ago. The early Earth atmosphere contained no free oxygen. The dating of the earliest biogeochemical processes associated with sulfur oxidation and the generation of acid drainage depends on the presence or absence of pyrite grains in nonmarine sedimentary rocks. Sulfur-reducing microbial communities may represent some of the earliest bacteria on Earth and may have existed near the dark, hot, nutrient-rich waters of hydrothermal vents in the oceans. The iron- and sulfur-oxidizing communities of bacteria and archaea developed later with the ability to obtain energy from the iron- and sulfur-oxidation process.

Acid drainage on the Earth's surface has been occurring naturally for eons. Iron sulfides, pyrite in particular, are common in organic-rich sediments, forming below the surface where hydrogen sulfide gas produced by sulfate-reducing bacteria reacts with iron dissolved in oxygen-depleted waters. Crystalline pyrite occurs in igneous and hydrothermal deposits as well. Even though pyrite and iron sulfides are common in rocks, they are almost never found in sediment grains formed when surficial rocks erode and create sedimentary deposits. This is because the pyrite would have been oxidized by the exposure to atmospheric oxygen as it is exposed and eroded on the surface of the Earth. Preserved pyrite found in sedimentary deposits is not common in modern nonmarine sediments after the Precambrian because sulfate levels tend to be very low, and free oxygen levels in the atmosphere allowed for generally aerobic conditions in surface waters. Therefore, the time at which pyrite and other oxygen-sensitive minerals, such as siderite (iron carbonate) and uraninite (uranium dioxide), are found in sedimentary rocks at a time of deposition reveals when the amount of oxygen in the atmosphere and surface ocean was small. The level of oxygen in the atmosphere is estimated to have an upper limit of about 1% of present-day 20.9% oxygen levels, and the oxygen level might have been much lower. About 2.2 to 2.3 billion years ago, the oxygen content in the atmosphere and oceans increased dramatically, probably associated with oxygen production by cyanobacteria: blue-green algae. After that time, pyrite, siderite, and uraninite have not been present as sediment grains on the surface of the Earth. Since pyrite would still have been available and eroded from surface source rocks over geologic time, the absence of pyrite as sediment grains some 2.2 to 2.3 billion years ago indicates the oxidation of iron sulfides and the beginning of sulfur oxidation on Earth and the earliest formation of the biogeochemical processes that produce acid drainage.

- What is the extent of acid drainage on Earth?

Based on the presence of the elements sulfur, oxygen, and iron in the solar system and the universe beyond, similar sulfide oxidation reactions, induced chemically or catalyzed by microbes, may possibly

to occur elsewhere in the solar system. In this book we describe the oxidation of sulfides and the ensuing consequences of these reactions: prediction, prevention, and remediation once these seemingly irreversible reactions start. Currently, acid mine drainage microbial communities are being documented in countless environmental settings on every continent, including Antarctica. Some of these are nonextreme environments with regard to temperature and pressure, and might be grass pasture soils or even agricultural soils. Examples of extreme environments where acid mine drainage microbial communities exist include high-temperature, high-pressure environments such as petroleum reservoirs and deep oceanic hydrothermal vents. The same sulfur streaks as those seen in the Rio Tinto area can also be seen in extreme environments such as on Ellesmere Island in the Canadian High Arctic, where research suggests that dark red smears are the result of sulfur-oxidizing metabolism by aerobic bacteria. Based on the literature, acid mine drainage microbial communities are relatively diverse and widespread on Earth.

- Is sulfur oxidation likely to occur outside Earth?

Acid drainage caused by sulfide oxidation is a universal process that is likely to be found in other locations in the solar system and beyond, possibly abiotically (using chemistry without microbes) or biotically with iron- or sulfur-oxidizing microbes. Iron-oxidizing microbes are more likely to be found than aerobic life forms in the search for life on other moons and planets, because free oxygen in oceans or in an atmosphere is not likely to exist unless it has been produced by microbes, as on Earth. In fact, it is possible that these same reactions might occur in places beyond Earth where these elements and compounds react together. Billions of years ago, sulfur-oxidizing reactions may have occurred on Mars. Europa, a moon of Jupiter, and Titan and Enceladus, two moons of Saturn, are believed to have liquid water. Several researchers have noted that the luminous white surface of Europa is stained dark red, possibly representing sulfur-rich deposits that could be by-products of sulfur oxidation.

In summary, acid drainage and sulfur oxidation are widespread and have a large impact on Earth's resources and are associated with environmental challenges. This book has brought together scientists and engineers who have independently researched acid mine drainage, acid rock drainage, and acid sulfate soils, to summarize our current knowledge in one volume.

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PART I
CAUSES OF ACID MINE DRAINAGE, ROCK DRAINAGE, AND SULFATE SOILS

1
ACID DRAINAGE AND SULFIDE OXIDATION: INTRODUCTION

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Since antiquity, and escalating on a large scale at the beginning of the industrial revolution, the extraction of coal, iron ore, and other minerals and metals from the Earth has had a significantly adverse impact on the environment. Acid mine drainage (AMD) or acid rock drainage presents one of mining's most serious threats to surface water and groundwater.

Introduction

The presence of acid mine drainage has the potential, and under certain conditions has actually devastated rivers, streams, and aquatic life for a very long time. Mineral resources such as coal, and metal ores such as gold, silver, and copper, are often rich in sulfide minerals, reflecting rock or sediment environments generally high in sulfur content and low or devoid of free molecular oxygen. Once exposed to water and air during mining, pyrite and other iron sulfide rocks release sulfuric acid in the presence of extremely acidophilic microorganisms. These complex interactions occur in microbial communities of autotrophic and heterotrophic bacteria and archaea which catalyze iron and sulfur oxidation, determining the release rates of metals and sulfur to the environment as acid mine drainage (Baker and Banfield, 2003). Even eukaryotic life forms (fungi and yeasts, protozoans, microalgae, and rotifera) may be part of microbial communities present in low-pH environments. Although the primary aerobic iron- and sulfur-oxidizing bacteria have been studied for decades, more recently, DNA analysis and genetic studies have identified some archaea, and even a few eukaryotes, to be present in the microbial community in the extremely low-pH acid mine drainage environments studied (Baker and Banfield, 2003). The ecology and biodiversity of acid mine and rock drainage microbial communities have been well documented by Baker et al. (2004, 2009) and Rawlings and Johnson (2002, 2007).

Once the sulfuric acid is created, the pyrite dissolves in drainage water, releasing associated metals and metalloids such as aluminum or arsenic into the surrounding environment. Wherever iron sulfides are exposed, such conditions can occur: open pits, underground excavations, leach pads, and tailing and waste rock piles.

Contaminated water flowing from abandoned coal mines is one of the most significant contributors to water pollution in former and current coal-producing areas. Acid mine drainage can have severe impacts on aquatic resources, can stunt terrestrial plant growth and harm wetlands, can contaminate groundwater, can raise water treatment costs, and can damage concrete and metal structures. In the Appalachian Mountains of the eastern United States alone, more than 7500 miles of streams are affected. The Pennsylvania Fish and Boat Commission estimates that the economic losses on fisheries and recreational uses are approximately $67 million annually. While most modern coal-mining operations must meet strict environmental regulations concerning mining techniques and treatment practices, there are thousands of abandoned mine sites in the United States.

Treatment of a single site can result in the restoration of several miles of affected streams. Acid runoff from the Summitville mine in Colorado, a designated federal Superfund site, killed all biological life in a 17-mile stretch of the Alamosa River. Acid and metals in runoff from the mining of molybdenum at the

Questa mine in New Mexico adversely affected biological life along 8 miles of the Red River. The effect on the environment can be severe. Streams and surface water bodies with a pH of 4.0 or lower can be devastating to fish, animals, and plant life. Once started, the process becomes very difficult to stop and can occur indefinitely, requiring mitigation and water treatment long after mining ends—in perpetuity. Along with countless other mines throughout the world featuring serious long-term environmental impacts, acid drainage at the Golden Sunlight mine is estimated to continue for thousands of years.

Common iron sulfide minerals, primarily pyrite (FeS_2), but also marcasite (FeS_2), arsenopyrite (FeAsS), and chalcopyrite ($CuFeS_2$), are exposed to the oxygen in the atmosphere during mining, excavation, or through natural erosion processes, and the compounds react with oxygen and water to form sulfate, resulting in acid drainage. This acidity results from the action of extremely acidophilic bacteria, which generate their energy by oxidizing ferrous iron [Fe(II) or Fe^{2+}] to ferric iron [Fe(III) or Fe^{3+}] using oxygen for cellular respiration. The ferric iron, in turn, dissolves the pyrite to produce soluble ferrous iron and sulfate. The ferrous iron is then available for oxidation by the aerobic acidophilic microbes, which scavenge dissolved oxygen in the pore space or water column. This biogeochemical cycle continues until the iron sulfide mineral (e.g., pyrite) is dissolved.

The oxidation of pyritic sulfur is a heat-generating reaction. In coal seams the pyrite oxidation reaction is sufficiently exothermic that mined-out areas in underground coal mines in high-sulfur-content coal seams have been documented to have had spontaneous combustion. The heat generated from the oxidation of pyritic sulfur can increase the temperature of the surrounding coal, increasing the rate of oxidation and causing coal degradation to occur (Smith et al., 1996). Excluding oxygen from the air in mined-out areas is the theoretical solution to spontaneous combustion related to pyrite oxidation, but in practice it is difficult to hermetically seal mined-out areas to exclude oxygen. Heat from the reaction can occur not only in subsurface mines but also in mine waste rock piles, where the heat is dissipated by thermal conduction or convection. Stability analysis of mine waste rock indicates that convective flow can occur because of the high porosity of the material. Convection cells formed in waste rock would draw in atmospheric air with oxygen and continue to drive the oxidation reaction. Convection gas flow due to the oxidation of sulfide minerals depends on the maximum temperature in the waste rock. The maximum temperature depends on the ambient atmospheric temperature, the strength of the heat source, and the nature of the upper boundary. If the sulfide waste is concentrated in one area, as is the case with encapsulation, the heat source may be very strong (U.S. Environmental Protection Agency, 1994). Due to the exothermic nature of the oxidation process, removing the oxygen from the pore spaces of sulfur-rich waste rock piles can minimize the chance for oxidation and combustion.

The hot exothermic reactions produce sulfuric acid–rich solutions which contain high concentrations of metals, frequently iron, aluminum, arsenic, lead, copper, cadmium, manganese, and zinc. Although this reaction can occur abiotically, it appears that most of the oxidation of sulfide minerals on Earth over the past more than 2 billion years since oxygen has been present in the atmosphere has occurred as a result of aerobic microbial-catalyzed processes on the reaction surfaces of iron sulfide minerals in the presence of atmospheric oxygen and water.

Early Earth Atmosphere

According to Cloud (1968), Knoll and Holland (1995), Baker and Banfield (2003), and Knoll et al. (2012), the environmental conditions of the early Earth were anoxic prior to the appearance of oxygen-producing bacterial photosynthesis. Before photosynthesis evolved in microbes, Earth's atmosphere had no free oxygen (O_2). In the Precambrian, early anaerobic sulfate-reducing microbes used the sulfate

(SO_4^{2-}) rather than free oxygen for respiration, and hydrogen sulfide (H_2S) was produced as the waste product (Schidlowski et al., 1983).

DNA-based studies of microbes populating mining environments containing acid mine drainage have provided insights into the diversity of acidophilic, metal-tolerant species. The broad distribution and ubiquitous nature of acidophiles associated with pyrite oxidation and acid mine drainage includes numerous nonextreme environments, including arid southwestern U.S. soil, Wisconsin agricultural soil, and grass pasture rhizospheres, to name a few locations. The extreme environments where acidophiles were identified included high-temperature petroleum reservoirs, a mid-Atlantic hydrothermal vent, a Yellowstone National Park hot spring, Antarctic sea ice and water, deep subsurface paleosol, and the Iron Mountain mine near Mt. Shasta, California. As well as acidophilic prokaryotes, such as iron- and sulfur-oxidizing bacteria and archaea, eukaryotic life forms (fungi and yeasts, protozoans, microalgae, and rotifera) may be active in environments where the pH is below 3, such as in waters produced by acid drainage. More information on bacteria, archaea, and eukaryotic life forms may be found in articles by Baker and Banfield (2003) and Rawlings and Johnson (2002). Microbial populations not only play a key role in acid drainage, but have also been identified in microbial-induced corrosion and in bioleaching for metal resources. Significantly improved understanding and control of diffusion processes on mineral surfaces in the nanoenvironment will help to minimize acid mine drainage, increase structural corrosion protection of industrial facilities, and raise yields of metal resource recovery in bioleaching processes.

Acid drainage, most of which is the result of isolated point sources of pyrite and other sulfide minerals that are exposed to water and oxygen in the atmosphere, can be removed through erosion within a few thousand to a few million years. With the large acidophile diversity and the limited duration of active acid drainage processes, many of which are isolated point sources, lateral gene transfer is a mechanism by which some AMD survival genes could be introduced to create new acid- and metal-tolerant lineages of organisms. There is no evidence to suggest that AMD organisms evolved from nonextremeophiles when local acidic environments appeared (Baker and Banfield, 2003). Mielke et al. (2003) have shown that acidic conditions can eventually develop through microbial activity by *Acidithiobaccilus ferrooxidans*, even though the initial pH conditions for microbial-induced pyrite oxidation were neutral.

Acid Drainage Deposits

Acid drainage deposits are found throughout the world in a variety of settings, including both natural environments and anthropogenic land disturbances such as highway construction and mining, where acid-forming sulfide minerals are exposed at the surface of the Earth (Jennings et al., 2008). Whether acid drainage occurs at coal mines, in hardrock metal ore deposits as a result of construction projects, in naturally occurring gossans, or in coastal marine sediments containing potential acid sulfate soils, it involves the complex interaction of an oxidizing agent, typically oxygen, with iron sulfide compounds, primarily pyrite, catalyzed primarily by acidophilic, metal-tolerant iron- and sulfur-oxidizing bacteria in the presence of water. Aerobic oxidation of iron, commonly called *rust*, does occur chemically without microbial involvement. The complete redox cycle with Fe(III) and Fe(II) shuttles electrons back and forth in energy transfer by microbial populations using different terminal electron acceptors. In a microbial process related to acid mine drainage, microbial-induced corrosion of iron and steel infrastructure affects nearly all industries, including water and sewage collection in cast iron pipes and the distribution of natural gas and oil in steel pipes. Building and bridge steel used for structural purposes undergoes constant microbial-induced corrosion attack if the steel and iron components are exposed to conditions favoring microbial activity.

Although abiotic oxidation of ferrous iron with oxygen can occur chemically at mine sites under suitable conditions, the majority of sulfuric acid generation related to pyrite oxidation is initiated and greatly accelerated by iron- or sulfur-oxidizing bacteria. Sulfide oxidation catalyzed by bacteria and other microbes may have reaction rates six orders of magnitude (i.e., 1 million times) greater than the same reactions in the absence of microbial communities (Evangelou and Zhang, 1995). Acid drainage generation is a complex biogeochemical process involving oxidation and reduction (even on the same mineral surface), hydrolysis, precipitation, and dissolution reactions as well as microbial catalysis (Nordstrom and Alpers, 1999). Early microbial research regarding bacteria and the acid drainage process originally identified *T. ferrooxidans* as the main iron-oxidizing bacteria. After genetic research and better laboratory procedures were developed to examine the presence of various microbes associated with the production of acid drainage, it is now known, based on DNA-based studies, that numerous other iron- and sulfur-oxidizing microbial species exist, which include bacteria and, to a lesser extent, archaea. In some cases, even small populations of prokaryotic organisms may also be present. Significant variations in the species diversity of microbial communities can exist between different sample locations. More detailed information on microbial communities in acid mine drainage may be found in the work of Baker and Banfield (2003).

The longevity of acid drainage proves that once pyrite oxidation catalyzed by microbial communities begins, it is virtually impossible to control the acid drainage without significant engineering effort. Consequently, many ancient pre-Roman mining sites are still producing acid drainage. Dioscorides, a Greek physician of the first century A.D., noted the presence of vitriol, an acidic liquid produced near copper ore deposits on Cyprus (Karpenko and Norris, 2002). The mine drainage was sulfuric acid associated with the oxidation of iron sulfide minerals with copper and other trace metals.

For European alchemists during the Middle Ages, sulfuric acid associated with metal mine drainage was called *oil of vitriol*. Vitriol was used in the production of acids, medicines, and leather dyes and is the source of the word *vitriolic,* which in common conversation means caustic speech or criticism that is extremely bitter. Vitriol is now known to consist of hydrated sulfates of iron, copper, and even magnesium and zinc, which are all secondary minerals associated with weathering of metallic sulfide deposits, commonly known at the time as pyrites.

Not only are sulfur-rich precipitates signs of acid drainage, but the formation of sulfuric acids also liberates associated metals, such as iron, aluminum, arsenic, zinc, lead, nickel, and copper, among other metals, into surface water and groundwater. Even mineral prospectors looked for the naturally occurring “yellow boy” signature of iron hydroxide in creek beds as evidence of nearby sulfur-rich metal ores. Although naturally occurring acid drainage exists, most major challenges relate to coal or metal mining, and the resulting damage to aquatic organisms, fish kills, and the environment as well as the destruction of water and plant resources is significant in certain parts of the world. It should be noted that not all coal or metal mines produce acid drainage, and not all acid drainage is produced by mines.

This book is a compilation or status report of what is known on the subject of pyrite oxidation and acid drainage, sometimes described in the highly fragmented scientific literature using different terms. When associated with coal or metal mining, sulfuric acid generation is referred to as *acid mine drainage* (AMD) and *mine-influenced water*. Acid generation without the anthropogenic influence of mining is frequently called *acid rock drainage* (ARD) in the literature, and in some countries, ARD refers to low-pH mine-related drainage. Acid sulfate soils form when iron sulfide minerals are exposed at the surface to produce sulfuric acid, iron oxides, iron hydroxides, and sulfate precipitates, as well as water runoff containing metals. The acid sulfate soils are usually acidic, with a pH below 3.0. Even though the term and locations of acid sulfate soils and, consequently, the literature differ from those of acid mine and rock

drainage, the microbial communities, the minerals, and the sulfide oxidization processes are virtually identical. The stoichiometry of pyrite oxidation as a chemical reaction is summarized as

$$FeS_2 + 3\tfrac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1.1)$$

Note that microbial catalysis is not featured in this reaction, even though it is accelerated greatly by microbial interactions with the pyrite.

Sulfide oxidation and acid generation with the associated metal mobilization are not limited to surface processes. A practical understanding of these complex biochemical reactions relates directly to groundwater resources as well. An example can be found in aquifer storage and recovery programs. Although aquifer storage and recovery should have little to do with acid mine drainage, the fact is that pyrite oxidation greatly affects subsurface water storage in some parts of the world. This is true of the important balancing of supply and demand of limited water resources in areas with growing populations and dwindling water supplies, such as Florida in the United States. Iron sulfide oxidation in the subsurface and the control of redox conditions and pH must be understood for aquifer storage and recovery. Strangely, the chemistry is similar to the acid mine drainage chemistry featured in reaction (1.1). Arsenic mobilization within subsurface storage aquifers is closely associated with the injection of oxygenated treated surface water into anoxic water zones containing iron sulfides. Chemical processes have been designed to remove the dissolved oxygen in injected waters, to prevent dissolution of the pyrite and mobilization of arsenic in areas where aquifer storage and recovery programs have been developed (Pearce and Waldron, 2011).

To integrate the successes and failures from different acid drainage prevention and control strategies, the various causes, assessment, prevention, remediation, and policies and regulations associated with the sulfide oxidation process have been reviewed and compiled to illustrate the range of approaches.

Resources from Acid Drainage

Sulfuric acid is the most abundantly produced chemical in the world. It is a strong acid, a strong oxidizing agent, and a good dehydrating agent. It is used in producing fertilizers, color dyes, petrochemicals, paints, plastics, lead–acid batteries, and detergents. It is also used in ore processing, steel manufacturing, oil refining, and wastewater processing. Treating acid drainage as a potential resource in appropriate economic conditions might open up the possibility of producing industrial-grade sulfuric acid, reclaiming metals solubilized in the acidic waters, and recovery of the water resource itself.

Water originating from coal mines in West Virginia in the eastern bituminous coal belt of the United States has been used to produce trout for the past few decades (Semmens and Miller, 2004; Miller, 2008). Treated water from acid mine drainage can also be reused as makeup water for the oil and gas shale fracturing process that is occurring in many parts of the Appalachian coal basins, including New York, Pennsylvania, West Virginia, Virginia, and other states that have large coal reserves. Shale gas wells such as those in the Marcellus Shale Formation in Pennsylvania require about 1 million gallons of carrier fluid, most of which is water. The water is used in the high-pressure rock-fracturing process to release the oil or gas trapped in the rocks. Acid drainage water that has been cleaned and treated using industrial processes can provide inexpensive recycled water in large volumes for this particular injection process.

In A.D. 166, the scientist Galen described what appears to be in situ leaching of minerals in an old copper and lead mine in Cyprus. In 1572, heap leaching of copper sulfides in Rio Tinto in Spain was documented. Bioleaching was first tried at Rio Tinto on low-grade ore in 1879. For bioleaching, bacteria

and archaea are used to recover metals, in particular copper and gold, from ores and concentrates. Having developed from a very simple operation in terms of both engineering and biology processes, biomining or bioleaching has developed into a multifaceted technology. Many of the largest industrial stirred tanks and heap leaching methods for sulfide ores throughout the world are used for bioprocessing minerals aboveground (Rawlings and Johnson, 2007). Bioleaching uses mixed cultures of acidophilic microorganisms for leaching generally low-grade sulfide ores of copper, nickel, zinc, uranium, and cobalt. Mining companies have been using bioleaching since the early 1980s. Bioleaching is a process of optimizing the biogeochemical processes on mine wastes and tailings piles to convert insoluble metal sulfides into water-soluble metal sulfates, such as copper sulfate. Mine tailings and waste rock might also be recycled into building materials such as aggregate rock in cement products or for creating recycled products, such as cold-mix asphalt, which could be used locally. For these types of mine waste recycling processes, significant engineering design and leachability testing are required. Enhancements to bioleaching can be made in optimizing the nanoenvironmental geochemistry to allow for a faster and more efficient exchange of terminal electron acceptors and nutrients in the microbial community. Microbial enhancements have been used for decades in the groundwater remediation industry, where aerobic, anaerobic, and co-metabolic microbial processes are optimized using a variety of in situ technologies and tools to deliver terminal electron acceptors, nutrients, and food, if needed.

Environmental Challenges

Not all mines and land disturbance create acid drainage. Maest et al. (2005) evaluated the methods for predicting future acid drainage generation for hardrock mines in the western United States based on environmental impact reports and other methods. Kuipers et al. (2006) provided the answer to the question of predictability of acid drainage prior to mining. The environmental challenges of predicting acid mine drainage are well documented in their work. They concluded that accurate prediction and active prevention of acid drainage are extremely difficult. Once acid drainage starts, stopping the biochemical process and returning to a predisturbance environment is virtually impossible.

The real environmental challenge in many countries will be to limit the acid drainage damage of existing orphan mine sites that are scattered over many countries on every continent. In these cases, there may be a surface pit where centuries ago gold was extracted and turned into art and jewelry, with the residual waste piles containing iron sulfide–rich rocks that produce sulfuric acid which continues to drain down the hillsides into nearby creeks and wetlands.

The Rio Tinto acid mine drainage in southern Spain illustrates the long duration, in human terms, of the biogeochemical acid drainage process. The Rio Tinto ore body was deposited in the Carboniferous period (about 359.2 million to about 299.0 million years ago) by hydrothermal activities on the seafloor under reducing conditions. The sulfur is contained in pyrite and other deposits through ground disturbance, the unoxidized pyrite crystals and other reduced sulfur compounds are catalyzed by the iron- and sulfur-oxidizing bacteria found on the surfaces of the sulfur minerals, and the generation of sulfuric acid is initiated. Rio Tinto means “red river,” reflecting the red and orange acid drainage color noted by early observers of the mining region.

Since ancient times, the metal resources in the Rio Tinto area have been mined for copper, gold, silver, and other minerals. About 3000 B.C., Iberians and Tartessians began mining the site near shallow metal deposits. Later, Phoenicians, Greeks, Romans, and Visigoths mined the site. The Moors also mined the Rio Tinto mineral deposits. After a period of abandonment, the mines were rediscovered in 1556 and the Spanish government began operating them again in 1724. The acid mine drainage, which has been ongoing

for about 5000 years despite recent efforts to curb the environmental damage, could continue for centuries to millions of years.

Putting sulfur and iron oxidation challenges in perspective, according to Kleinmann (1989) and to Lyon et al. (1993) there may be as many as 500,000 inactive or abandoned mines in the United States, with acid mine drainage severely affecting about 19,300 km^2 of streams and more than 7200 ha of lakes and reservoirs (Gagliano and Bigham, 2006). In many abandoned mine sites, there are no responsible parties to remediate the sites, and most governmental agencies and countries are unlikely to have adequate funding for these cleanup needs.

Future Opportunities

Future mining and development projects can, however, be evaluated for possible water quality impacts. Risk assessment should be part of acid generation prediction evaluation to better define the risks and uncertainties of a particular project. Community and stakeholder input should be part of the evaluation process as well. Acid drainage mitigation measures, strict regulations, and rigorous field monitoring and testing can be put in place to limit environmental damage. As more demand for access to mineral resources occurs over time, environmental stewardship and resource recovery of the acid drainage resources must become standard business practice for sustainable mining operations. The increasingly large scale of new mines or mine expansions planned in unpopulated or wilderness areas will push political debates in Alaska and other areas as to the benefits of job creation, the control of mining wastes, the production of acid mine drainage, and the protection of water resources and wildlife. In potential mining areas with indigenous populations, mining areas may contain sites having significant historical, cultural, and spiritual values. For sustainable mineral production, these complex and divisive issues will need to be addressed.

Observations and research being conducted at abandoned mines has provided considerable opportunity to reevaluate existing mining operations and practices and to promote a healthy mining industry complemented by environmental protection. The most important issue facing the industry is the cause of long-term environmental impact and how such impacts can be avoided. Concepts for closure and closure design have come a very long way since the 1950s, and the current focus is on how physical and chemical stability can be achieved. The editors and authors are confident that this volume will make a positive contribution to the discussion.

References and Suggested Reading

Agricola, G., 1556. De Re Metallica. Translated in 1912 by H.C. Hoover, and L.H. Hoover. Republished by Dover, New York, 1950, 572 pp.

Baker, B.J., and Banfield, J.F., 2003. Microbial communities in acid mine drainage. FEMS Microbiology Ecology, vol. 44, pp. 139–152.

Baker, B.J., Lutz, M.A., Dawson, S.C., Bond, P.L., and Banfield, J.F., 2004. Metabolically active eukaryotic communities in extremely acidic mine drainage. Applied and Environmental Microbiology, vol. 70, no. 10, pp. 6264–6271.

Baker, B., Tyson, G., Goosherst, L., and Banfield, J., 2009. Insights into the diversity of eukaryotes in acid mine drainage biofilm communities. Applied and Environmental Microbiology, vol. 75, no. 7, p.

2192.

Cloud, P., 1968. Atmospheric and hydrospheric evolution of the primitive earth. Science, vol. 160, pp. 729–736.

Center for Streamside Studies, 2002. Environmental Impacts of Hardrock Mining in Eastern Washington. College of Forest Resources and Ocean and Fishery Sciences, University of Washington, Seattle, WA.

Evangelou, V.P., and Zhang, Y.L., 1995. A review: pyrite oxidation mechanisms and acid mine drainage prevention. Critical Reviews in Environmental Science and Technology, vol. 25, no. 2, pp. 141–199.

Gagliano, W.B., and Bigham, J.M., 2006. Acid mine drainage. In: Encyclopedia of Soil Science. CRC Press, Boca Raton, FL.

Jennings, S.R., Neuman, D.R., and Blicker, P.S., 2008. Acid Mine Drainage and Effects on Fish Health and Ecology: A Review. Reclamation Research Group Publication, Bozeman, MT, 26 pp.

Karpenko, V., and Norris, J.A., 2002. Vitriol in the history of chemistry. Chemické Listy, vol. 96, pp. 997–1005.

Kleinmann, R.L.P., 1989. Acid mine drainage in the United States: controlling the impact on streams and rivers. In: 4th World Congress on the Conservation of Built and Natural Environments, Toronto, ON, Canada, pp. 1–10.

Knoll, A.H., 2003. Life on a Young Planet: The First Three Billion Years of Evolution on Earth. Princeton University Press, Princeton, NJ, 277 pp.

Knoll, A.H., and Holland, H.D., 1995. Oxygen and Proterozoic evolution: an update. In: Effects of Past Global Change on Earth, Panel on Effects of Past Global Change on Life, eds. National Academy of Sciences, Washington, DC.

Knoll, A.H., Canfield, D.E., and Konhauser, K.O., eds., 2012. Fundamentals of Geobiology. Wiley-Blackwell, Chichester, UK. 443 pp.

Konheiser, K.O., 2006. Introduction to Geomicrobiology. Wiley-Blackwell, Chichester, UK. 440 pp.

Kuipers, J.R., Maest, A.S., MacHardy, K.A., and Lawson, G., 2006. Comparison of Predicted and Actual Water Quality at Hardrock Mines: The Reliability of Predictions in Environmental Impact Statements. Kuipers & Associates, Butte, MT, 228 pp.

Lane, N., 2009. Life Ascending: The Ten Great Inventions of Evolution. W.W. Norton, New York, 344 pp.

Lyon, J.S., Hilliard, T.J., and Bethel, T.N., 1993. Burden of Guilt. Mineral Policy Center, Washington, DC, 68 pp.

Maest, A., Kuipers, J., Travers, C., and Atkins, D., 2005. Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties, and State-of-the-Art. Kuipers & Associates, Butte, MT, 90 pp.

Mielke, R.E., Pace, D.L., Porter, T., and Southam, G., 2003. A critical state in the formation of acid mine drainage: colonization of pyrite *Acidithiobacillus ferrooxidans* under pH-neutral conditions. Geobiology, vol. 1, pp. 81–90.

Miller, D., 2008. Using aquaculture as a post-mining land use in West Virginia. Journal of the

International Mine Water Association, vol. 27, no. 2, pp. 122–126.

Nordstrom, D.K., and Alpers, C.N., 1999. Geochemistry of acid mine waters. In: The Environmental Geochemistry of Mineral Deposits, Part A, Processes, Methods, and Health Issues, G.S. Plumlee, and M.J. Logsdon eds. Reviews in Economic Geology, vol. 6A. Society of Economic Geologists, Littleton, CO, pp. 133–160.

Pearce, M.S., and Waldron, M., 2011. Addressing the mobilization of trace metals in anearobic aquifers. In: Proceedings of the 2011 Georgia Water Resources Conference, April 11–13, University of Georgia, Athens, GA, 5 pp.

Rawlings, D.E., and Johnson, D.B., 2002. Ecology and biodiversity of extremely acidophilic microorganisms. In: Encylopedia of Life Support Systems, vol. 3, Extremeophiles. EOLOS Publishers, Oxford, UK, 36 pp.

Rawlings, D.E., and Johnson, D.B., 2007. Biomining. Springer-Verlag, New York, 334 pp.

Russell, M., 2006. First life. American Scientist, vol. 94, pp. 32–39.

Russell, M.J., and Martin, W., 2004. The rocky roots of the acetyl CoA pathway. Trends in Biochemical Sciences, vol. 29, pp. 358–363.

Russell, M.J., Hall, A.J., and Gize, A.P., 1990. Pyrite and the origin of life. Nature, vol. 344, p. 387.

Russell, M.J., Hall, A.J., and Martin, W., 2010. Serpentinization and its contribution to the energy for the emergence of life. Geobiology, vol. 8, pp. 355–371.

Schidlowski, M., Hayes, J.M., and Kaplan, I.R., 1983. Isotopic inferences of ancient biochemistries: carbon sulfur, hydrogen, and nitrogen. Earth's Earliest Biosphere, In: J.W. Schopf, ed. Princeton University Press, Princeton, NJ, pp. 149–186.

Semmens, K., and Miller, D., 2004. Utilizing mine water for aquaculture: an overview of production formats. Abstracts, American Society of Mining and Reclamation, Morgantown, WV, April 18–22.

Smith, A.C., Rumancik, W.P., and Lazzara, C.P., 1996. SPONCOM: a computer program for the prediction of the spontaneous combustion potential of an underground coal mine. In: Proceedings of the 5th Conference on the Use of Computers in the Coal Industry, S.D. Thompson, R.L. Grayson, and Y.J. Wang, eds., West Virginia University, Morgantown, WV, January, pp. 134–143.

U.S. Environmental Protection Agency, 1994. Acid Mine Drainage Prediction. EPA 530-R-94-036, NTIS PB94-201829. U.S. EPA, Washington, DC, 52 pp.

2
VITRIOLS IN ANTIQUITY

STEPHEN M. TESTA

Vitriols have played a very important role in the development of modern chemistry and metallurgical practice, and have engaged the attention of many alchemists and mineralogists (Kappenko and Norris, 2002). Fundamentally, *vitriol* is defined as a sulfate of any of various metals, such as copper, iron, or zinc, and especially a hydrate of such a sulfate (heptahydrate or pentahydrate) having a glassy appearance or luster (American Geological Institute, 1996). All vitriols are poisons. Historically, the terminology surrounding vitriol and the pyrites can be confusing, as the mineralogy and chemistry are in their infancy.

Introduction

The presence of vitriols is found to be of chemical and mineralogical interest in European, Indian, and Arabic alchemy (Kappenko and Norris, 2002). Early recognition of vitriol was as a commodity, not as a focus of environmental concern and abatement. Georgius Agricola (also known as Georg Bauer, 1494–1555) does note one of the earliest adverse environmental effects of vitriol (native zinc sulfate or goslarite, as defined by Dana). It is mentioned briefly by Agricola (on page 215 of his *De Natura Fossilium*, which was published in 1546 and represented the first scientific attempt to categorize minerals, rocks, and sediments since the publication of Pliny the Elder's *Naturalis Historia*. Agricola makes reference to an acrid solidified juice that commonly comes from cadmia: “At Annaberg in the tunnel driven to the Saint Otto mine; it is hard and white, and so acrid that it kills mice, crickets, and every kind of animal. However, that feathery substance that oozes out from the mountain rocks and the thick substance found hanging in tunnels and caves from which saltpeter is made, while frequently acrid, does not come from *cadmia*” (Hoover and Hoover, 1912).

The earliest familiarity with vitriol is shown by a Sumerian word list dating from around 600 B.C., in which types of vitriol are listed by color (Crosland, 1962). The earliest surviving discussions of vitriol are from the works of the Greek physician Dioscorides (ca. A.D. 40 to 90; Gunther, 1959) and the Roman naturalist Pliny the Elder (A.D. 23 to 79), author of *Naturalis Historia*, published around A.D. 77 to 79. Dioscorides first mentions the later-Latinized terms *chalcitis* (cuperious pyrites), *misy* (mine vitriol), *sory*, and *melanteria* (Hoover and Hoover, 1912). These are all native minerals, whereas vitriol can be native or artificial. Both authors describe vitriol as white dripstones in caves, mine tunnels, and along the sides of pits in the vicinity of copper ore deposits on Cyprus.

The ubiquitous bright yellow-to-orange staining found in rivers and creeks from naturally occurring sulfide oxidation processes was undoubtedly known to early humans. Our more curious human ancestors might have looked to see if there were any usable resources associated with these discolorations. By the time of Assurbanipal, an Assyrian king (668 to 626 B.C.), chemical lists included substances recognized today as metallic sulfides and sulfates. Pliny the Elder noted metal mining in his *Naturalis Historia*, and he was undoubtedly familiar with the signs of acid drainage associated with Roman mine workings. Acid mine drainage continues to emanate from mines in Europe established during the Roman Empire prior to A.D. 467 (Center for Streamside Studies, 2002). Pliny believed that blue vitriol (i.e., copper sulfate pentahydrate) could be congealed from evaporating certain springs (inferred to be mine drainage water)

in parts of Spain and on the island of Cyprus. Melanteria, or inkstone, was probably a sulfate of iron formed in a matrix containing vegetable astringent matter, which in combination produced a natural ink (Moore, 1834).

The longevity of acid drainage proves that once pyrite oxidation begins, it is virtually impossible to control the drainage without significant engineering effort. The mine drainage noted was sulfuric acid associated with the oxidation of iron sulfide minerals with copper and other trace metals. Pedanius Dioscorides (ca. A.D. 40 to 90) was a Greek physician, pharmacologist, and botanist, and the author of *De Materia Medica* (Regarding Medical Materials). This five-volume encyclopedia about herbal medicine and related medicinal substances (a pharmacopeia) was widely read for more than 1500 years. Dioscorides, the first to note vitriol, an acidic liquid produced near copper ore deposits on Cyprus, is credited with the first adequate description of vitriol:

> Vitrio (chalcanthon) is of one genus, and is a solidified liquid, but it has three different species. One formed from the liquids which trickle down drop by drop and congeal in certain mines,; therefore those who work in the Cyprian mines call it *stalactis*. Petesius calls this kind *pinarion*. The second kind is that which collects in certain caverns; afterwards it is poured into trenches, where it congeals, whence it derives its name *pectos*. The third kind is called *hephthon* and is mostly made in Spain; it has a beautiful colour but is weak. …

These sulfates were often characterized by striking blue and green crystals, and their distinctive chemical properties are in modern times recognized as hydrated sulfates of iron, copper, magnesium, and zinc. The iron and copper varieties of iron and copper were widely recognized and used in antiquity. In mineralogical terms, the green and blue vitriol correspond to the minerals melanterite ($FeSO_4 \cdot 7H_2O$) and chalcanthite ($CuSO_4 \cdot 5H_2O$), respectively. These varieties were known to form spectacular crystals of a vitreous luster but were also known to occur more commonly in botryoidal, granular, or stalactitic masses. In the more common forms, crystals were reported in dull shades of blue or yellow, or as being completely white. Highly soluble and prone to degradation by absorbing water, their occurrence was ephemeral.

Georg Bauer, known by his Latinized pen name, Georgius Agricola, published *De Re Metallica* (On the Nature of Metals) in 1556, the first important treatise on mining metal ores and refining and smelting metals. It exhibits detailed woodcut illustrations not only of the mechanics of sixteenth-century mining, but also of the devastation of streams by acid drainage (Jennings et al., 2008). The book remained the authoritative text on mining for almost two centuries. In 1912, the first English translation of *De Re Metallica* was published privately in London and sold by subscription. Of note, the translators were Herbert Hoover, a mining engineer and later President of the United States and his wife, Lou Henry Hoover, a geologist and Latin scholar.

Vitriol Terminology

In antiquity, sulfides that formed as secondary minerals within the weathering zones of metallic sulfate deposits were referred to as *pyrites*. Stones called pyrites and malores by Pliny the Elder were sometimes common compact limestones; however, the name *pyrites* was not confined to millstone but was applied to various minerals that produced sparks on percussion, such as sulfuret of iron, with which pyritous copper was confused (Dioscorides describes pyrites as a species of stone from which copper is melted) (Moore, 1834).

The Persian physician and alchemist Muhammed ibn Zakkarija as-Razi (ca. A.D. 854 to 925/935)

recognized six atraments (metallic sulfates and their impurities). As-Razi is credited with recognition of vitriol as a special group exhibiting compositional similarities and chemical relationships between these substances (Karpenko and Norris, 2002), as shown in Table 2.1. Agricola divided vitriol into three types: white, green, and blue (i.e., zinc, iron, and copper sulfate hydrate, respectively; Hoover and Hoover, 1912). Examples of white, green, and blue vitriol presented by Sowerby (1804–1817) are illustrated in Figure 2.1a, b, and c, respectively. Agricola is credited by Hoover and Hoover (1912) as being the first person to mention white vitriol (zinc sulfate).

Table 2.1 Atraments Recognized by as-Razi

Black Atrament	**Impure $FeSO_4$**
Alum	Includes $KAI(SO_4)$ as well as other metallic sulfates
Calcandis	White atrament; weathering product of copper/ iron ores or alum
Calcande	Green atrament; iron and/or copper sulfate
Calcatar	Yellow atrament; decomposition of product of sulfide—sulfate-rich copper/iron ores, and burned iron vitriol or iron oxide
Surianum	Red atrament; same as calcatar

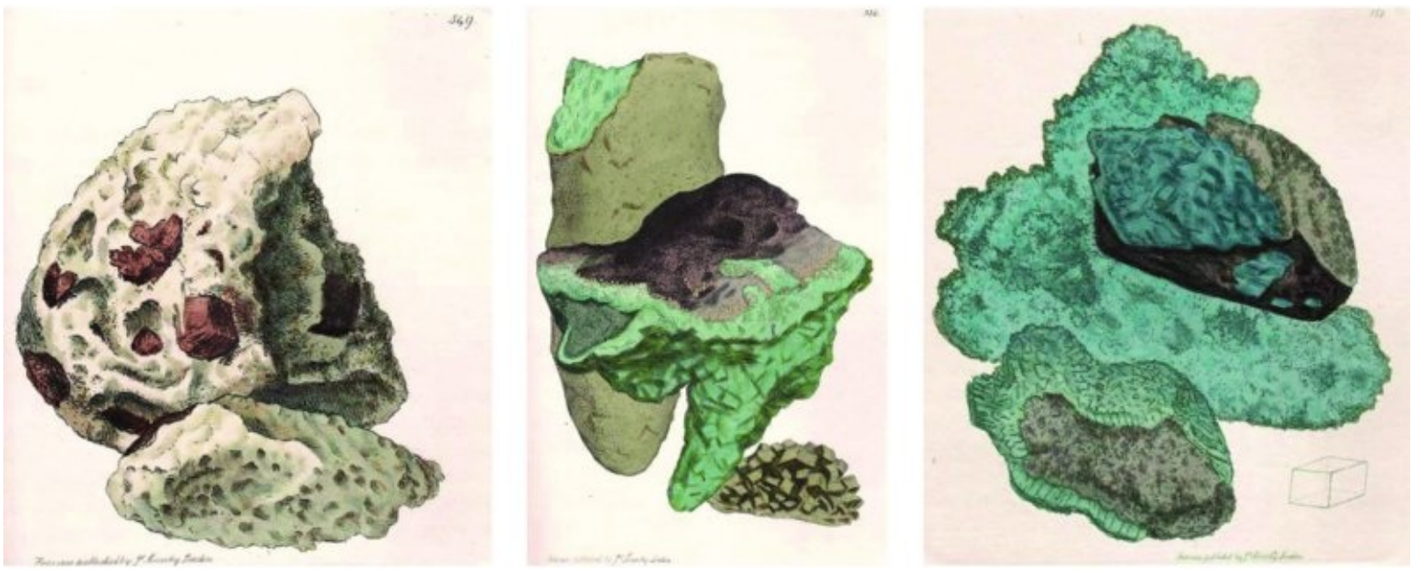


FIGURE 2.1 (a) Zincum sulfatum, sulfate of zinc, from Holywell in Flintshire, and distinguished from sulfate of iron, or copper, by its whiteness; commonly called white vitriol or white copperas (Sowerby, 1804, Table 349). Soluble in twice its weight of cold water, with a strong styptic taste. In its pure form it consists of oxide of zinc (40%), water (39.5%), and sulfuric acid (20.5%). (b) Ferrum sulphatum, sulfate of iron, or green martial vitriol from Cornwall, North Wales (lower figure) (Sowerby, 1804, Table 350). Used for making ink. Often of a fair green color. Kirwin analysis is oxide of iron (28%), water (46%), and sulfuric acid (26%). (c) Cuprum sulphatum, sulfate of copper, or blue vitriol from North Wales (Sowerby 1804, Table 351). Less soluble than sulfate of iron, requiring four times its weight of cold water and twice its weight of boiling water for solution, and styptic to taste. Kirwin analysis is oxide of copper (40%), sulfuric acid (31%), and water (29%). (Courtesy of the Testa Geological Heritage Library.)

For European alchemists during the Middle Ages, sulfuric acid associated with metal mine drainage was called *oil of vitriol*. We now know vitriol to be hydrated sulfates of iron, copper, and even magnesium and zinc, which are all secondary minerals associated with weathering of metallic sulfide deposits, commonly known at the time as pyrites. The term *vitriol* became more restrictive: by the sixteenth century referring mostly to sulfides with a metallic luster that yielded little or no metal. Other minerals were included with pyrite under this expansive term. For example, the Arabic name *marcasite* was commonly used synonymously with *pyrites* in much of the literature of the sixteenth century. It is speculated that in the course of mining such sulfides, vitriol was noted. Agricola's work toward a systematic treatment of mineralogy was followed by that of others. J.F. Henckel, chief director of the mines at Freiberg in Saxony, considered one of the leading mineralogist of the eighteenth century, addressed practically all the sulfide minerals in his *Pyritologia* (Henckel, 1852) (Figure 2.2). James Dwight Dana (1813–1895), the leading American mineralogist of his time, published five editions of his *A System of Mineralogy* … (1837–1868), with later editions edited by others. In the first (1837), second (1844), and third (1850) editions, Dana attempted to place minerals into a classification scheme similar to that of Lineaus's genus–species categories used in botany and zoology. It was not until 1854 when J.D. Dana published the fourth edition of *A System of Mineralogy* (1854) that he struck upon the chemical classification system (elements, sulfides, oxides, silicates, etc.) that we accept universally today. Dana's (1850) third edition works recognized seven forms of vitriol, as shown in Table 2.2.

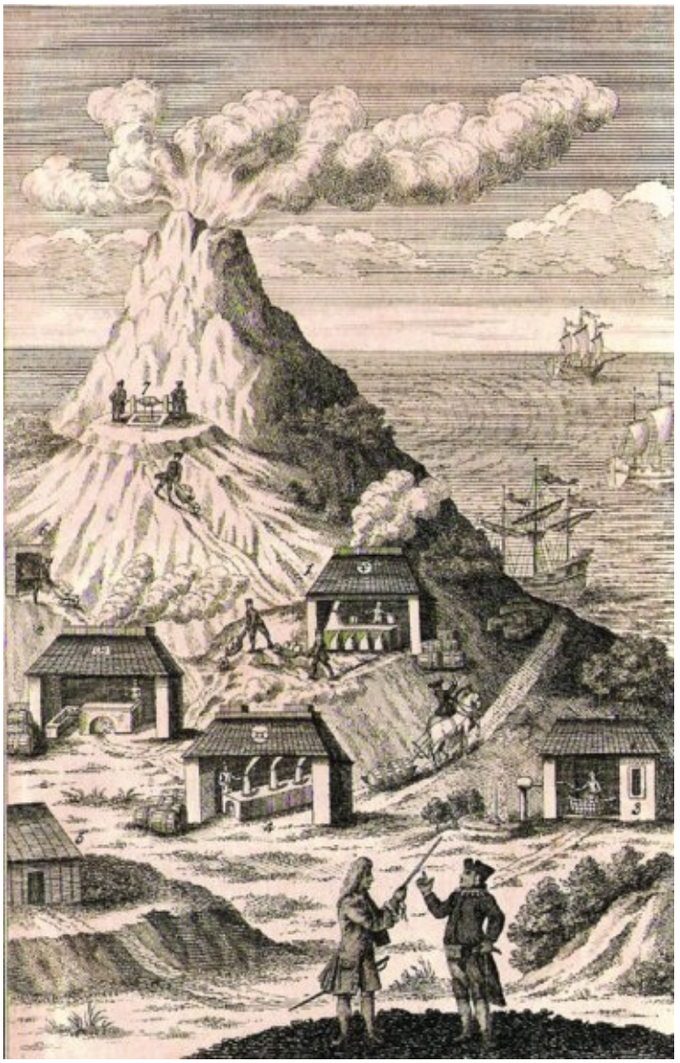


FIGURE 2.2 In Henckel's explanation of the frontispiece of his book *Pyritologia: or, a History of the Pyrites*, exhibited is a sulfur hut, with reverberating furnace and retorts, in which sulfur is driven or forced out of the pyrites (1). In the vitriol hut the leaden pan in which vitriol is boiled out of the pyrites with a washing trough is shown (2). The third hut shows desulfurated pyrites ilixiviated and prepared for making vitriol (3). In the arsenic hut stands the reverberating furnace with the dishes and subliming vessels out of which arsenic is forced (4). A coe or hut exists over the opening of the shaft (5). A level tunnel (6) and shaft (7) are also shown. Hot baths, volcanoes, and whirlpools are noted as deriving their matter from pyrites and sulfur. (From Henckel, 1852. Courtesy of the Testa Geological Heritage Library.)

Table 2.2 Vitriol Terminology by the Nineteenth Century[a]

Mineral Name	Synonyms	Occurrence	Location
Blue vitriol	Cyanose, sulfate of copper, Kupfervitriol; prismatic vitriol (Jameson, 1821); vitriol de cobre (Lucas, 1813)	Found in waters issuing from mines and in connection with rocks containing copper pyrites, by the decomposition of which it is formed.	Lead mines of Missouri (Schoolcraft, 1819). Rammelsberg mine near Goslar in the Hartz Mountains; Fahlun in Sweden, Pary's mine in Anglesea and in Wicklow; Rio Tinto in Spain; copper mines of Wicklow in Ireland (Jameson, 1821).
Cobalt vitriol	Bieberite, red vitriol, sulfate of cobalt, Kobaltvitriol, rhodalose	In rubbish of old mines.	Bieber, near Hanau, and Leogang in Saltzburg.
Green vitriol	Copperas, Eisen-vitriol, sulfate of iron, andmelanterite; hemiprismatic, fer sulfate or rhomboidal vitriol (Jameson, 1812); brongniart (Cleaveland, 1822)	Decomposition of iron pyrites, which readily affords it if moistened occasionally while exposed to the atmosphere.	Copperas Mountain near Bainbridge, Ohio; coal mines throughout the United States, and iron and coal mines in Europe and Asia (Jameson, 1821); Warren County in Tennessee and near East Andover, Maine (Cleaveland, 1822).
Lead vitriol	Anglesite, sulfate of lead, Bleivitriol, Vitriolbleierz	Decomposition of galena.	In the United States, the lead mines of Missouri; Southhampton, Massachusetts; Rossie, New York; Walton gold mine, Virginia; and Phenixville and Perkiomen, Pennsylvania; also, Leadhills, Wanlockhead, Pary's mine in Anglesea, Mellanoweth in Cornwall, Clausthal and Zellerfeld in the Hartz Mountains, and Badenweiler in Breisgan, among other localities.
Red-Iron vitriol	Botryogen (bunch of grapes), neoplase, rother vitriol, fer sulfate	Associated with copper mines.	Copper mines of Fahlun in Sweden.
White vitriol or zinc vitriol	Goslarite, sulfate of zinc, zinc sulfate, Zinkvitriol	Supposed to be formed by the decomposition of blende.	Rammelsberg mine in the Hartz Mountains, at Schemnitz in Hungary, at Fahlum in Sweden, and at Holywell in Wales; lead mines of the Arkansas Territory (Schoolcraft, 1819); of rare occurrence in nature; Cornwall (Cleaveland, 1822).

Source: Adapted from Dana (1850), Jameson (1821), Cleaveland (1822), and Lucas (1813).

[a] Much confusion is noted when referring to the mineralogical literature of the early nineteenth century. For example, Jameson (1821) refers to red vitriol or sulfate of cobalt as Kobaltvitriol. Cleaveland (1822) refers to Kupfervitriol as blue vitriol and to rhomboidal vitriol and bronhniart as sulfate of iron or copperas. Lucas (1813) refers to vitriol de cobre as cuivre silfate or blue vitriol.

Early terminology commonly referred to the pyrites as atrament and vitriol, which in modern parlance refer to the sulfates of divalent metals, principally iron and copper. Pliny the Elder described a process by which cords suspended in vats containing water impregnated with vitriol caused the accumulation of vitreous clusters of a remarkable luster, “vitrumque esse creditor,” hence the terms *vitriol* and *vitriolic*. The Greeks would call vitriol by the name *chalcanthon*; in Latin it was called *atramentum sutorium*, in reference to its use as a blackening agent for leather. Vitriol was first mentioned by Albertus Magnus (1193/1206–1280), also known as Albert the Great and Albert of Cologne, a German Dominican friar and bishop who achieved fame for his comprehensive knowledge of, and advocacy for, the peaceful coexistence of science and religion. Magnus is credited with the discovery of arsenic. He used the expression *atramentum viride a quibusdam vitreolum vicatur* (Hoover and Hoover, 1912).

Uses for Vitriol

Commercially, earthy masses and solutions of decomposing sulfide and sulfate minerals were extracted in ancient times. Vitriol was used in the production of acids, medicines, and leather dyes and is the source of the word *vitriolic*, which in common conversation means caustic speech or criticism that is extremely bitter. Since the blackening of leather could only be accomplished using iron-rich vitriol, iron-rich vitriol was used in antiquity regardless of its association with copper deposits. Commercial vitriol was obtained through lixivation techniques, described by Agricola in his *De Re Metallica* (Hoover and Hoover, 1912). Other uses included as leather and fabric dyes, in medical applications (notably for the eyes), metallurgical processes in the purification of gold and fabrication of imitation precious metals, as a flux for assay and smelting, and in alchemy (Karpenko and Norris, 2002).

Vitriol was a fundamental ingredient in the manufacture of all strong acids in antiquity. Also serving as a base ingredient for making strong acids, the discovery of nitric acid is estimated to have taken place sometime after 1300, about 200 years before it appeared in print. By the mid-sixteenth century, nitric acid was commonly used. One of four of Agricola's recipes included the following ingredients: “four librae of vitriol, two and a half librae of saltpeter, half a libra of alum, and one and a half librae of spring water.” His third recipe was the basis for the modern techniques of manufacturing sulfuric acid today (Figure 2.3). Agricola's third recipe is described as follows:

By the third method vitriol is made out of *melantria* and *sory*. If the mines give an abundant supply of *melanteria* and *sory*, it is better to reject the *chalcitis*, and especially the *misy*, for from these the vitriol is impure, particularly from the *misy*. These materials having been dug and thrown in to the tanks, they are first dissolved with water; then, in order to recover the pyrites from which copper is not rarely smelted and which forms a sediment at the bottom of the tanks, the solution is transferred to other vats, which are nine feet wide and three feet deep. Twigs and wood which float on the surface are lifted out with a broom made of twigs, and afterward all the sediment settles at the bottom of this vat. The solution is poured into a rectangular leaden caldron eight feet long, three feet wide, and the same in depth. In this caldron it is boiled until it becomes thick and viscous, when it is poured into a launder, through which it is run into another leaden caldron of the same size as the one described before. When cold, the solution is drawn off through twelve little launders, out of which it flows into as many wooden tubs four and a half feet deep and three feet wide. Upon these tubs are placed perforated crossbars distant from each other from four to six digits, and from the holes hang thin laths, which reach to the bottom, with pegs or wedges driven into them. The vitriol adheres to these laths, and within the space of a few days congeals into cubes, which are taken away and put into a chamber having a sloping board floor, so that the moisture which drips from the vitriol may flow into a tub beneath. This solution is re-boiled, as is also that solution which was left in the twelve tubs, for, by reason of its having become too thin and liquid, it did not congeal, and was thus not converted into vitriol.

FIGURE 2.3 The making of vitriol: A, wooden tub; B, crossbars; C, laths; D, sloping floor of the chamber; E, tub placed under the vitriol. [From Agricola, Book XII; (Hoover and Hoover, 1912); courtesy of the Testa Geological Heritage Library.]

Throughout the eighteenth century, sulfuric acid, oil of vitriol, could only be made by dry distilling minerals. The process, similar to the original alchemical processes, was to heat pyrite (iron disulfide, FeS_2) in air to form iron(III) sulfate [$Fe_2(SO_4)_3$], which when heated to 480°C decomposed to iron(III) oxide and sulfur trioxide, which passing through water yielded varying concentrations of sulfuric acid.

References and Suggested Reading

American Geological Institute, 1996. Dictionary of Mining, Mineral and Related Terms, 2nd ed. In cooperation with the Society of Mining, Metallurgy and Exploration, Englewood, Co, 646 pp.

Biringuccio, V., 1942. The Pirotechnia. Translated from the Italian with an Introduction and Notes by C.S. Smith and M.T. Gnudi. American Institute of Mining and Metallurgical Engineers, Englewood, Co, 476 pp.

Center for Streamside Studies, 2002. Environmental Impacts of Hardrock Mining in Eastern Washington. College of Forest Resources and Ocean and Fishery Sciences, University of Washington, Seattle, WA.

Cleaveland, P. 1822. An Elementary Treatise on Mineralogy and Geology. … Cummings and Hilliard, Boston, 818 pp.

Crosland, M.P., 1962. Historical Studies in the Language of Chemistry. Heinemann, London, 448 pp.

Dana, J.D., 1850. A System of Mineralogy Comprising the Most Recent Discoveries … , 3rd ed. George P. Putnam, New York, 711 pp.

Gunther, R.T., ed., 1959. The Great Herbal of Dioscorides. Hafner Publishing, New York, pp. 639–641.

Henckel, J.F., 1852. Pyritologia: or, a History of the Pyrites, the Principal Body in the Mineral Kingdom. … Translated from the German. London, 376 pp.

Hoover, H.C., and Hoover, L.H., 1912. Georgius Agricola's De Re Metallica. Translated from the first Latin edition of 1556 with biographical introduction, annotations and appendices. … London, 637 pp.

Jameson, R., 1821. Manual of Mineralogy Containing an Account of Simple Minerals, and Also a Description and Arrangement of Mountain Rocks. Hurst, Robinson and Company, Edinburgh, UK, 501 pp.

Kappenko, V., and Norris, J.A., 2002. Vitriol in the history of chemistry. Chemicke Listy, vol. 96, pp. 997–1005.

Kirwin, R., 1794. Elements of Mineralogy, 2nd ed., vol. 11. J. Nichols, London, 529 pp.

Lucas, J.A.H., 1813. Tableau methodique des especes minerales, 2nd partie. D'Hautel, Paris, 587 pp.

Moore, N.F., 1834. Ancient Mineralogy: or, an Inquiry Respecting Mineral Substances Mentioned by the Ancients: With Occasional Remarks on the Uses to Which They Were Applied. New York, 187 pp.

Pryce, W., 1778, A Treatise on Minerals, Mines and Mining. … London, 331 pp.

Schoolcraft, H.R., 1819. A View of the Lead Mines of Missouri: Including Some Observations on the Mineralogy, Geology, Geography, Antiquities, Soil, Climate, Population, and Productions of Missouri and Arkansas, and Other Sections of the Western Country. Charles Wiley and Company, New York, 299 pp.

Sowerby, J., 1804–1817. British Mineralogy: or, Coloured Figures Intended to Elucidate the Mineralogy of Great Britain. London.

3
BIOGEOCHEMISTRY OF ACID DRAINAGE

JAMES A. JACOBS AND DAVID B. VANCE

We begin this chapter with the sulfur cycle on a global scale, then look at smaller and smaller scales and the associated complexity within which iron sulfide oxidation occurs. From a coal-mining site where rainwater percolates onto the land surface and migrates into the subsurface, the focus migrates down to the sediments and rocks and later into the pore openings between pyrite mineral surfaces. Smaller still, the nanoenvironment scale is described where bacteria such as *Acidithiobacillus ferrooxidans*, a common rod-shaped acidophile, exists. At the scale of a bacterium, electrons are transferred in a series of redox reactions to energize iron- and sulfide-oxidizing microbes. Various microbial processes, the generation of acid drainage under pH-neutral conditions, and genetic studies are reviewed.

Acid Drainage Overview

On a global scale, sulfur is cycled throughout Earth, in all the media, including in the solid, liquid, and vapor phases. Figure 3.1 summarizes the large-scale sulfur cycle. A generalized global flux of sulfur and sulfur compounds was prepared by Stumm and Morgan (1996), and since then others have studied the large-scale sulfur cycle, including Schlesinger (1997), Andreae and Rosenfeld (2008), and Schlesinger and Bernhardt (2013). The global sulfur flux is shown graphically in Figure 3.2.

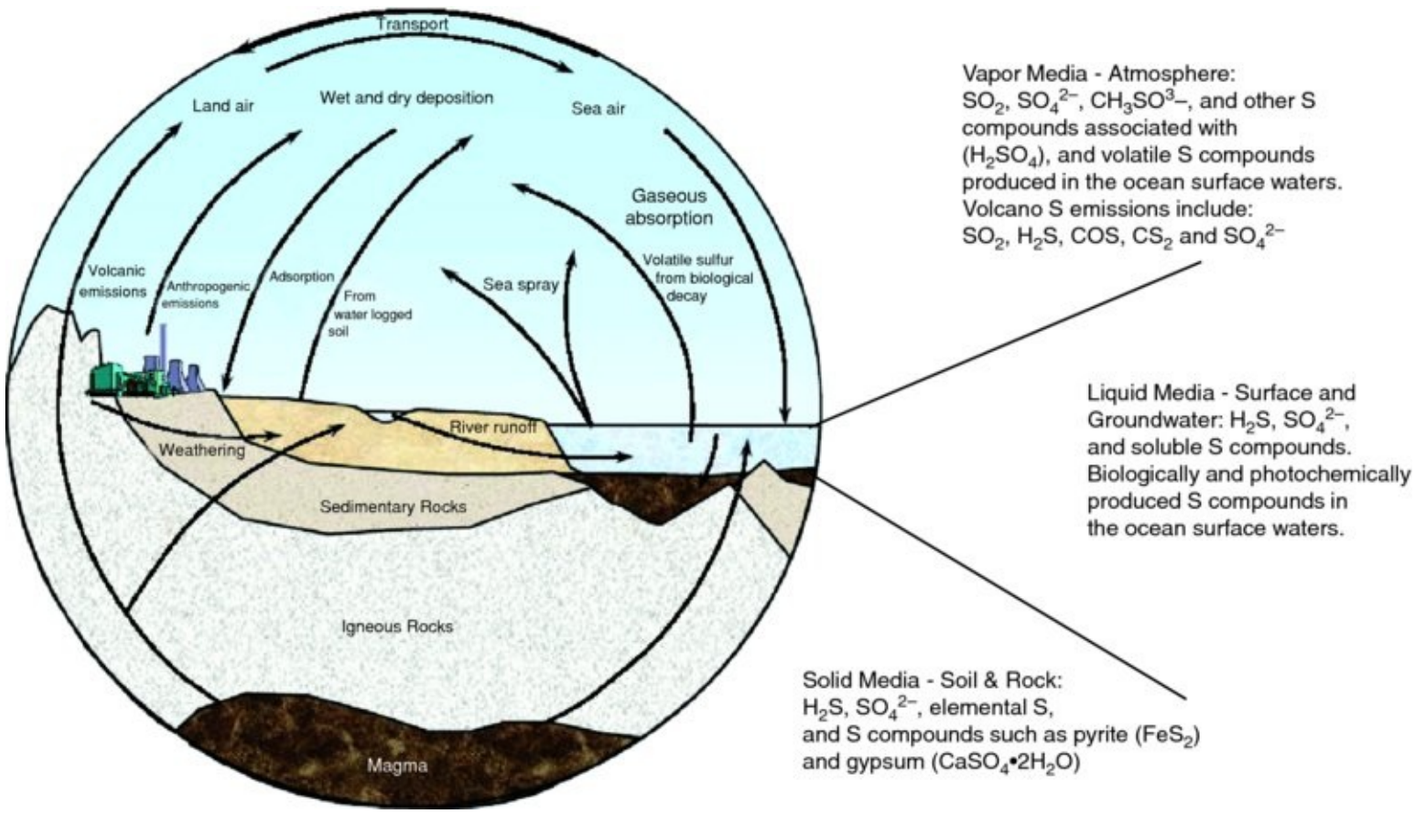


FIGURE 3.1 Large-scale sulfur cycle showing global sources of natural and anthropogenic sulfur emissions. (Modified after Ober, 2002.)

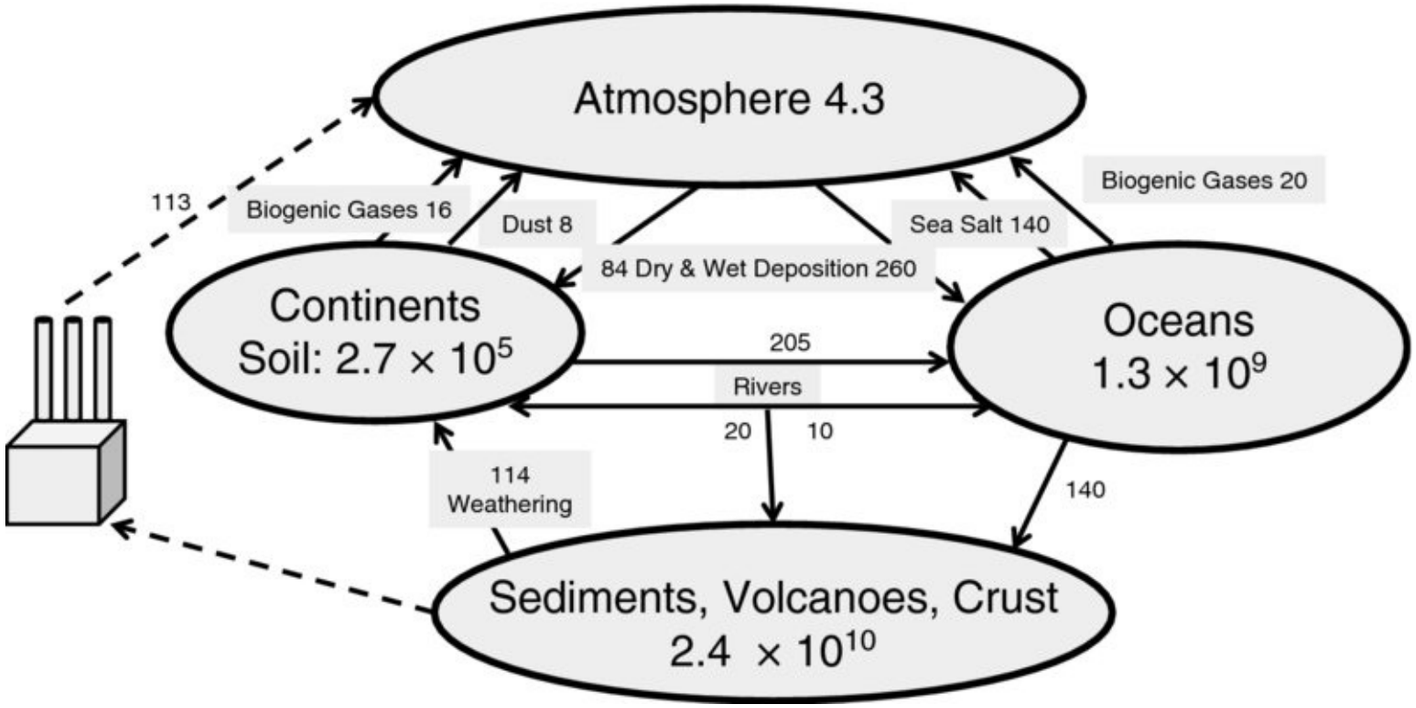


FIGURE 3.2 Global sulfur cycle showing global fluxes in millions of tons of sulfur per year and inventories in millions of tons of sulfur. (Modified after Stumm and Morgan, 1996.)

Scale of Acid Drainage

Although microorganisms are active in nanoenvironments, the scale of visible acid drainage impacts can be on the order of a few square feet for a small waste rock soil stockpile. A major mining operation, an extensive highway project through an environment with acid sulfate soils, or a large hillside grading project in pyrite-rich rocks, can affect countless acres. To put scale into perspective, a cross section at a large coal mine setting is shown in Figure 3.3. Rainwater in the figure is shown migrating through an underground mine, a strip mine, and a mine waste rock stockpile or spoil pile. Ultimately, the rainwater discharges into a stream. The figure illustrates the difficulty in controlling rainwater and groundwater and the challenges of limiting atmospheric oxygen to microbial populations in large areas with exposure to pyrite-rich rocks and sediments.

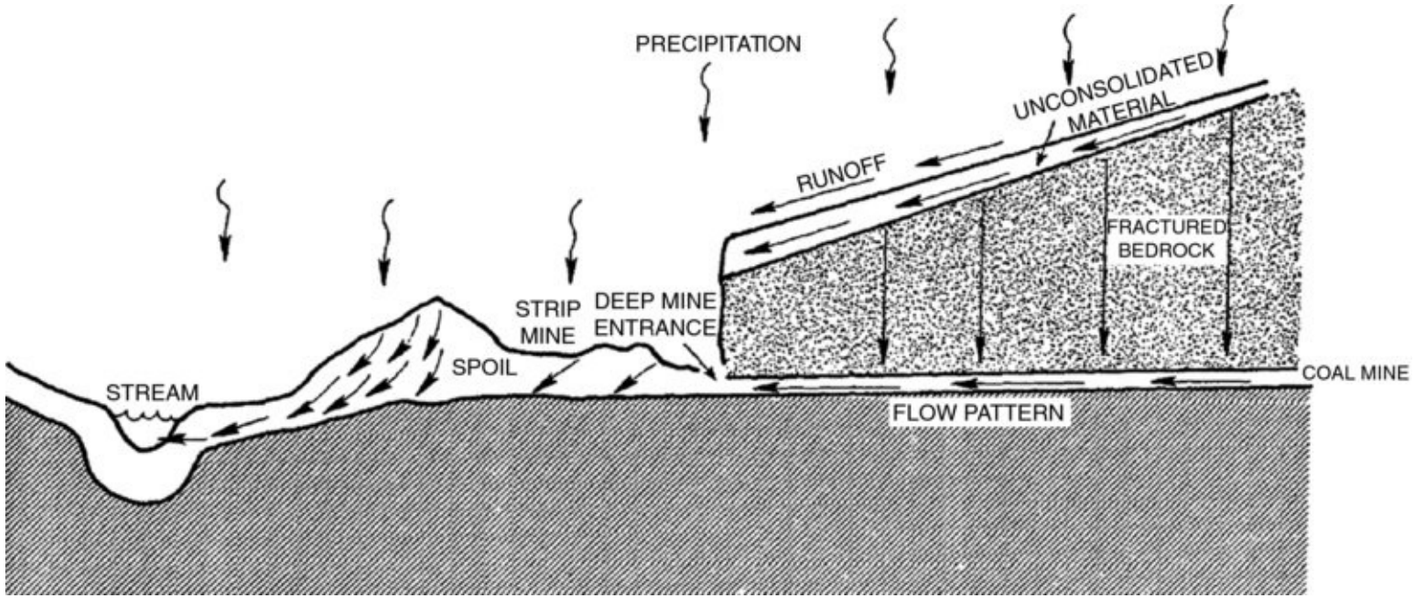


FIGURE 3.3 Rainwater migrating through an underground coal mine and strip mine. (After U.S. Environmental Protection Agency, 1977.)

Contrary Creek in Virginia is in an area containing a variety of abandoned base-metal massive sulfide mines and quartz–gold vein deposits. A location for producing over 6 million tons of pyrite ore is now noted as a site of acid mine drainage. The precipitation of “yellow boy” deposits is a signature of the result of acid drainage and is strong physical evidence of iron- and sulfide-oxidizing bacteria (Figure 3.4).

FIGURE 3.4 Contrary Creek, Virginia, showing an iron-rich precipitate containing sulfur. Many iron-oxidizing bacteria, such as *Thiobacillus thiooxidans* and *T. ferrooxidans*, produce deposits known as "yellow boy." (Courtesy of N. Robbins, U.S. Geological Survey.)

On a smaller scale, the conceptual cross section of the subsurface consisting of shallow soil or sediment (Figure 3.5) shows unsaturated and saturated zones, both of which can have an abundance of pyrite minerals, widespread iron- and sulfide-oxidizing microbial communities, pore water, and oxygen. When temperatures, nutrients, salinity, pressure, and other conditions are optimal, sulfide and iron oxidation catalyzed by microbial communities will occur. Pyrite and other iron sulfide minerals may be present in a variety of geological settings and forms. A schematic close-up of the saturated zone shows some of the saturated pore openings between sediment grains or rock fractures that could create a nanoenvironment for the initiation of pyrite oxidation (Figure 3.6). An example of the forms of minerals containing iron and sulfur include various mineral compounds, as well as concretions, sedimentary grains, crystals such as pyrite framboids, and finely disseminated pyrite. Iron monosulfide (FeS)–rich layers in exposed alluvial deposits in Oklahoma show an example of a layered sedimentary deposit (Figure 3.7a), and an image of framboidal pyrite illustrates an example of crystal morphology as well as intergranular porosity (Figure 3.7b).

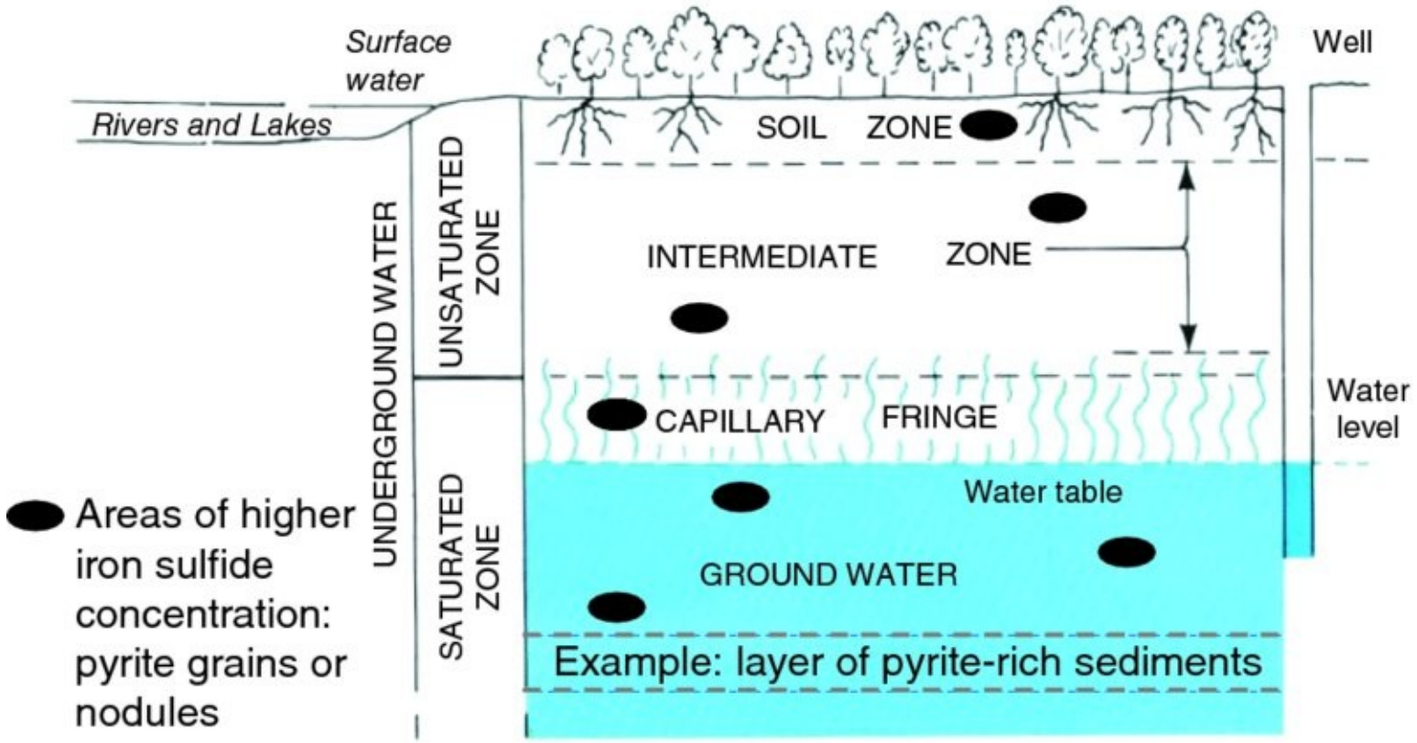


FIGURE 3.5 Shallow soil or sediments. Not to scale. (Modified after Heath, 1983.)

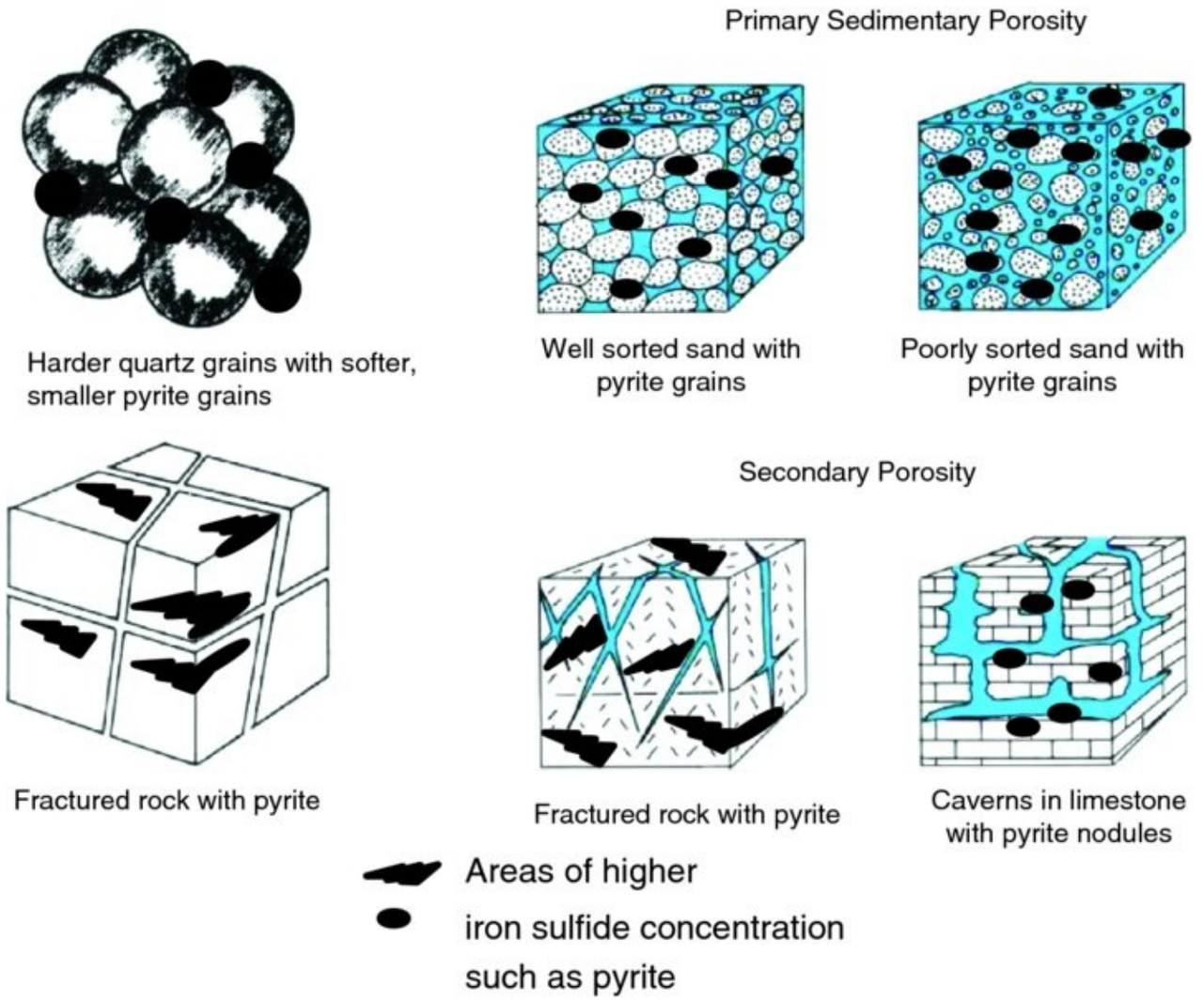


FIGURE 3.6 Close-up of subsurface environments that may support microbial life in the saturated zone. Not to scale. (Modified after Heath, 1983.)

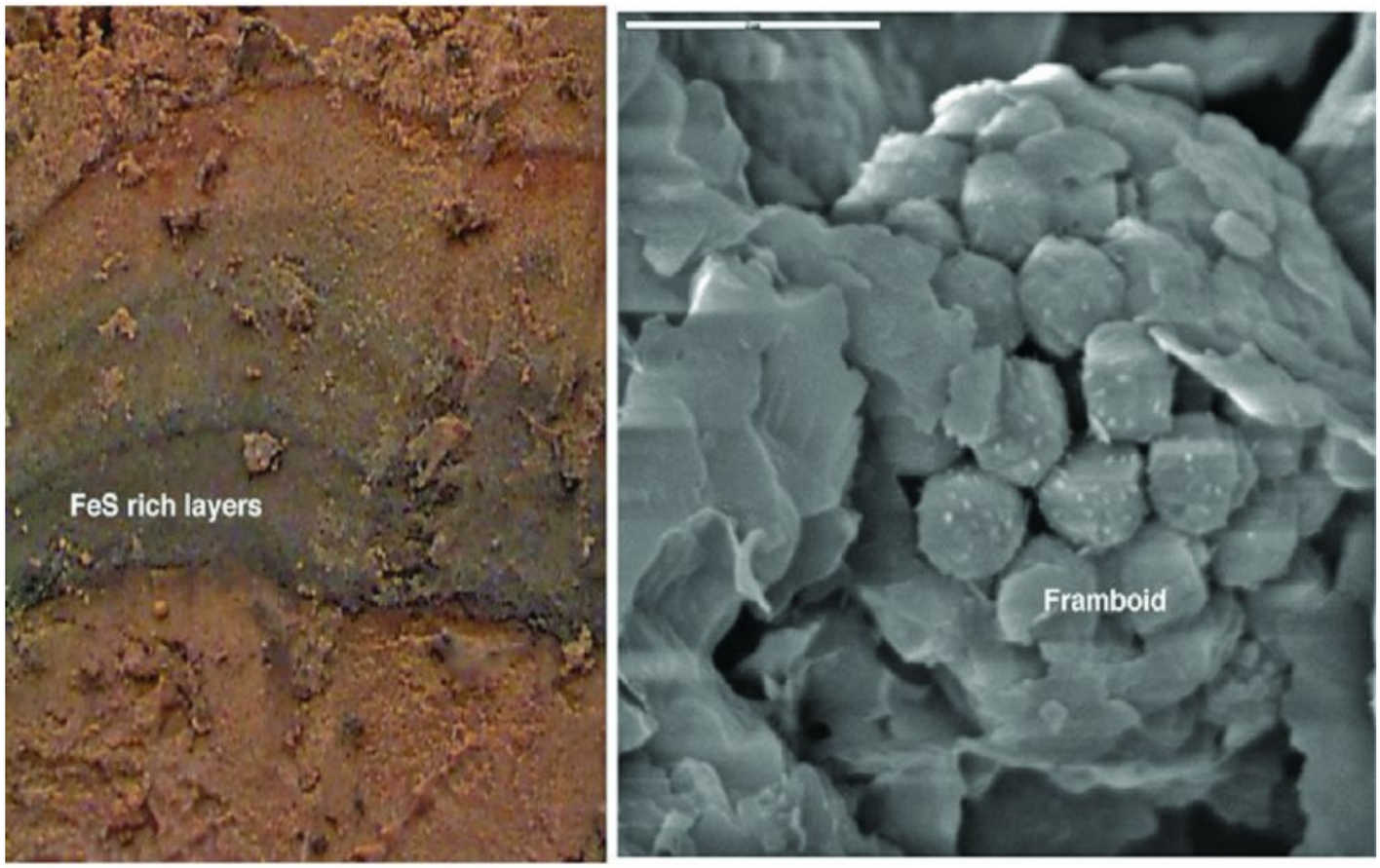


FIGURE 3.7 Iron–monosulfide layers in surface layers of alluvium at a Norman landfill site (a) and framboidal pyrite in the saturated zone (b). (Courtesy of M. Tuttle and G. Breit, respectively, U.S. Geological Survey.)

The unsaturated zone, also called the *vadose zone*, describes the environmental conditions at strip mines with waste rock stockpiles or excavations above the groundwater table. In waste rock stockpiles or in the unsaturated zone, limited pore water surrounding sediment grains with dissolved oxygen may coexist with adjacent oxygen in air pockets in the pore spaces, contributing to conditions for microbial oxidation of pyrite and other iron sulfide mineral surfaces (Figure 3.8). Microbes also require a carbon source for growth, heterotrophs need organic carbon as a source, and autotrophs must have carbon dioxide to support growth. Atmospheric carbon dioxide is sufficient, but additional carbon dioxide is often available in these systems, potentially stimulating growth further. Many of the microbes that are involved in acid mine drainage are autotrophic. Similar conditions are also created in underground mines or tunnels, where large open areas of atmospheric oxygen are in contact with subsurface water and iron sulfide minerals.

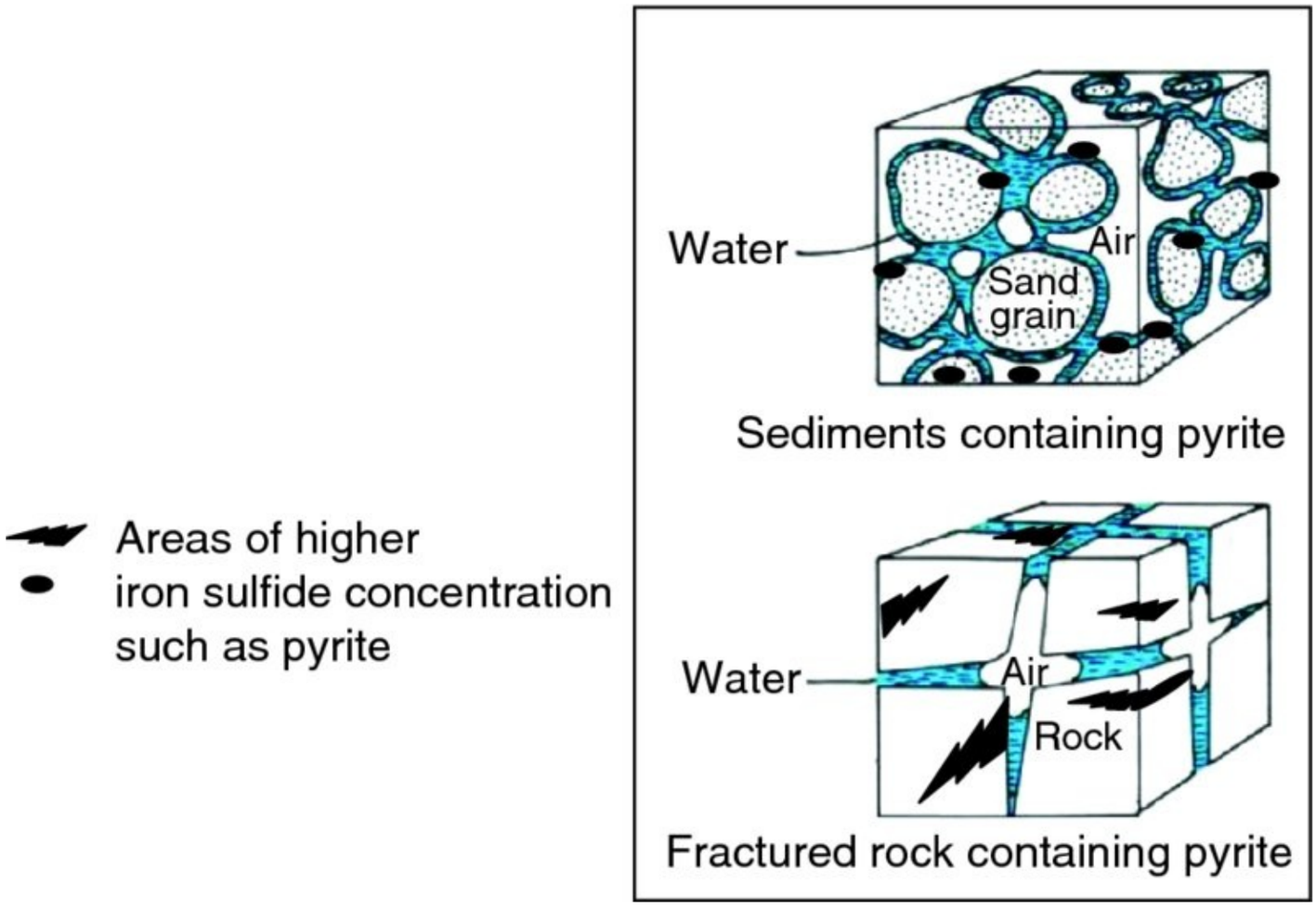


FIGURE 3.8 Environment in the unsaturated zone containing both some pore water and air pockets in the pore spaces. Not to scale. (Modified after Heath, 1983.)

Microbially Generated Acid Mine Drainage

Microbially generated acidic drainage is caused by the chemolithotrophic oxidation of reduced sulfur compounds in rocks, sediments, and soils by acidophilic prokaryotes in water, such as *Acidithiobacillus*, *Leptospirillum*, and *Ferroplasma*. These prokaryotes can be broadly divided into two distinct groups, bacteria and archaea. Acid drainage is the natural chemical reaction, which can proceed when iron disulfide (FeS_2), commonly known as pyrite, and other iron sulfides are exposed to water in the presence of oxygen in the atmosphere or with oxygen dissolved in the water in the presence of an otherwise anoxic environment. All microbes need water to survive. Even moisture in the presence of oxygen in air can initiate the oxidation of pyrite in the pore spaces of acid sulfate soils, pyrite-rich rock piles, sulfide ore mine waste tailings, or reduced sulfur-rich unsaturated zone soils. Although the reactions that generate sulfuric acid can proceed abiotically (see Figure 3.9), the biologically catalyzed reactions increase the sulfide oxidation rate by several orders of magnitude. As part of the exothermic microbial process, increased temperature of the environment also increases acidophilic metabolic rates and consequently increases sulfide oxidation rates as well. In some acid mine drainage systems, temperatures can reach 117°F (47°C), and the pH as low as −3.6, as seen in the Richmond mine Superfund site at Iron Mountain near Mt. Shasta in northern California (Nordstrom et al., 2000).

Membership in microbial communities varies with pH and temperature, mineralogy, and metals concentrations (Baker and Banfield, 2003). The phylogenetically diverse microbes tend to gather in

selective and opportunistic communities that can control the flow of food, nutrients, and energy. Collectively, each successful community identified by DNA-based studies controls the flow of iron, sulfur, nitrogen, carbon, and energy in different temperature regimes. For less than 30°C, *Thiobacillus* spp., *Acidithiobacillus* spp., *Thiobacillus* spp., and *Acidiphilum* spp. were identified together in the cycling of resources and energy, ultimately creating several reactions that, in sequence in a nanoenvironment, oxidize pyrite. A second microbial community was documented at 30 to 50°C: *Ferroplasma* spp., *Leptospirillum* spp., *Sulfobacillus* spp., and *Eukaruotes*. In the higher temperatures, greater than 50°C, *Metallosphaera* spp., *Sulfobacillus* spp., and *Themoplasma* spp. were identified by Baker and Banfield (2003).

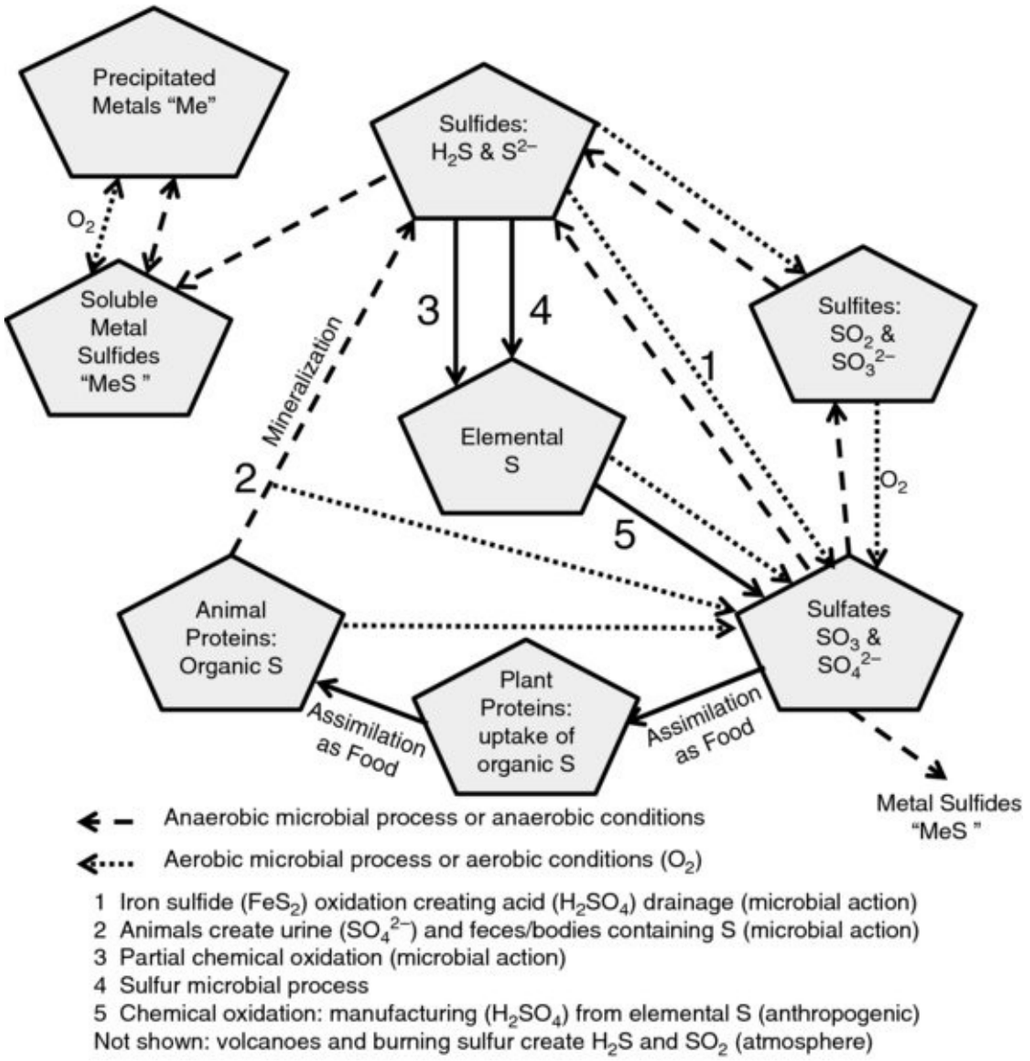


FIGURE 3.9 Some general small-scale sulfur reactions.

Small-Scale Sulfur Reactions

On a smaller scale from the global sulfur cycle (see Figure 3.1), a schematic of some of the general small-scale sulfur reactions is shown in Figure 3.9. The microbial sulfur cycle is highly complex and described in more detail by Canfield and Farquhar (2012). Although sulfur reactions can occur abiotically, many of the microbial sulfur reaction rates are catalyzed by actions of microorganisms (Figure 3.10). The physical evidence of acid mine drainage is visible to the naked eye at the scale of a small pool near Contrary Creek, Virginia (Figure 3.11). In this case, microbial action was identified in the field by an oil-like biofilm. The figure shows a scientist in the field using a color chart to identify specific colors of the

biofilm and associated acidic waters. The Munsell color system divides colors into hue, value, and chroma and is used by a variety of biologists, soil scientists, and geologists to identify colors in the field. Oil-like biofilms are sampled in the field and analyzed in the laboratory using microscopic imaging techniques and genetic analysis tools. This particular biofilm was produced by a colony of rod-shaped acidophilic microbes. In the study of biofilms, which commonly represent a community of varied microorganisms, a variety of imaging tools are used, including the confocal scanning laser microscope. Based on laboratory studies of growing a biofilm between two quartz glass plates and introducing a nutrient solution and inoculating with *Pseudomonas aeruginosa*, Brydie et al. (2004, 2009) showed the architecture of a microbial biofilm (Newman et al., 2012). A schematic of the biofilm architecture (Figure 3.12) shows the complex and symbiotic ecosystem that exists in microbial nanoenvironments. In terms of scale, the distance from the top of the mineral surface to the top of the biofilm carapace was measured at 25.3 µm.

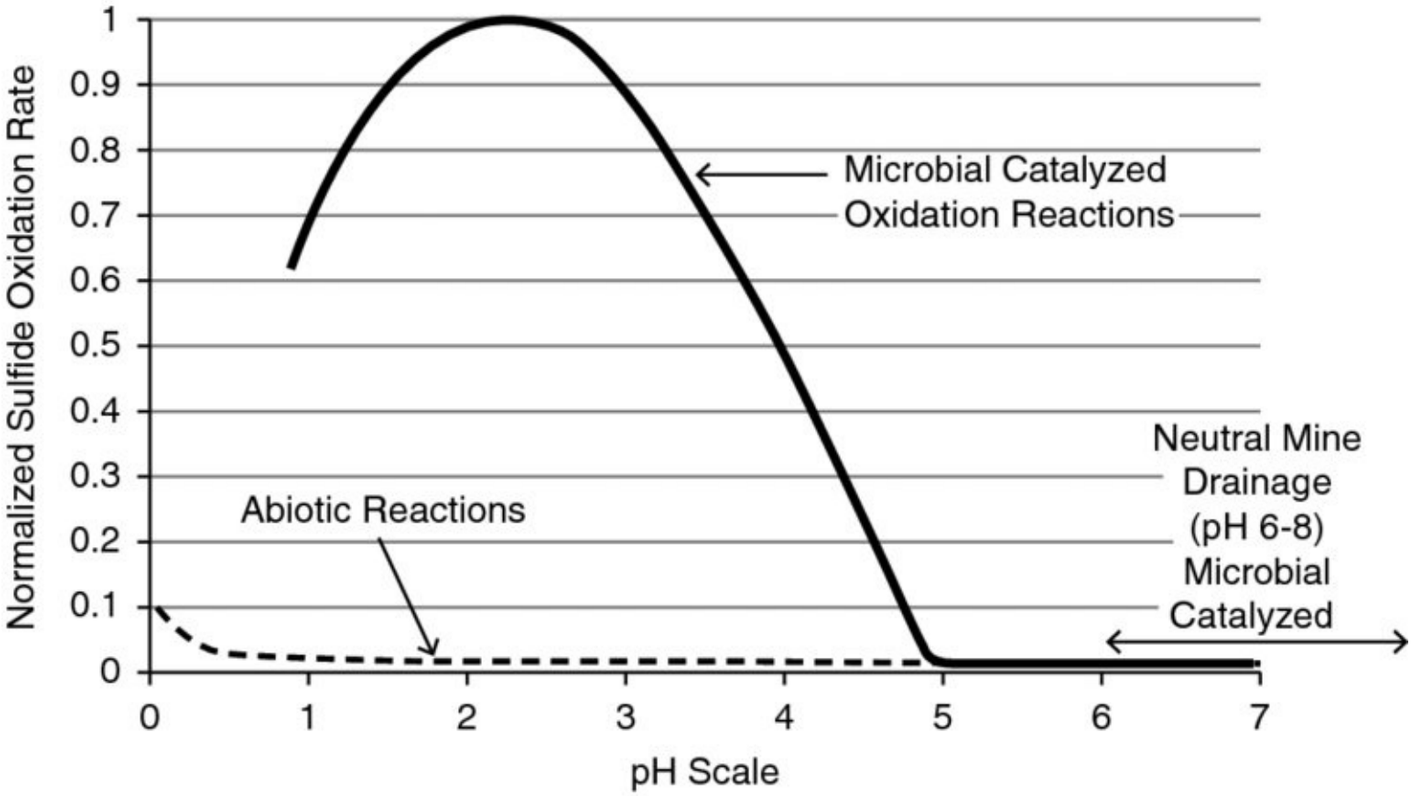


FIGURE 3.10 Normalized sulfide oxidation rates with and without microbial-catalyzed reactions. (Modified after Robertson and Broughton, 1992.)

FIGURE 3.11 Oil-like biofilm at Contrary Creek, Virginia, floating on acid water. (Courtesy of N. Robbins, U.S. Geological Survey, 2012.)

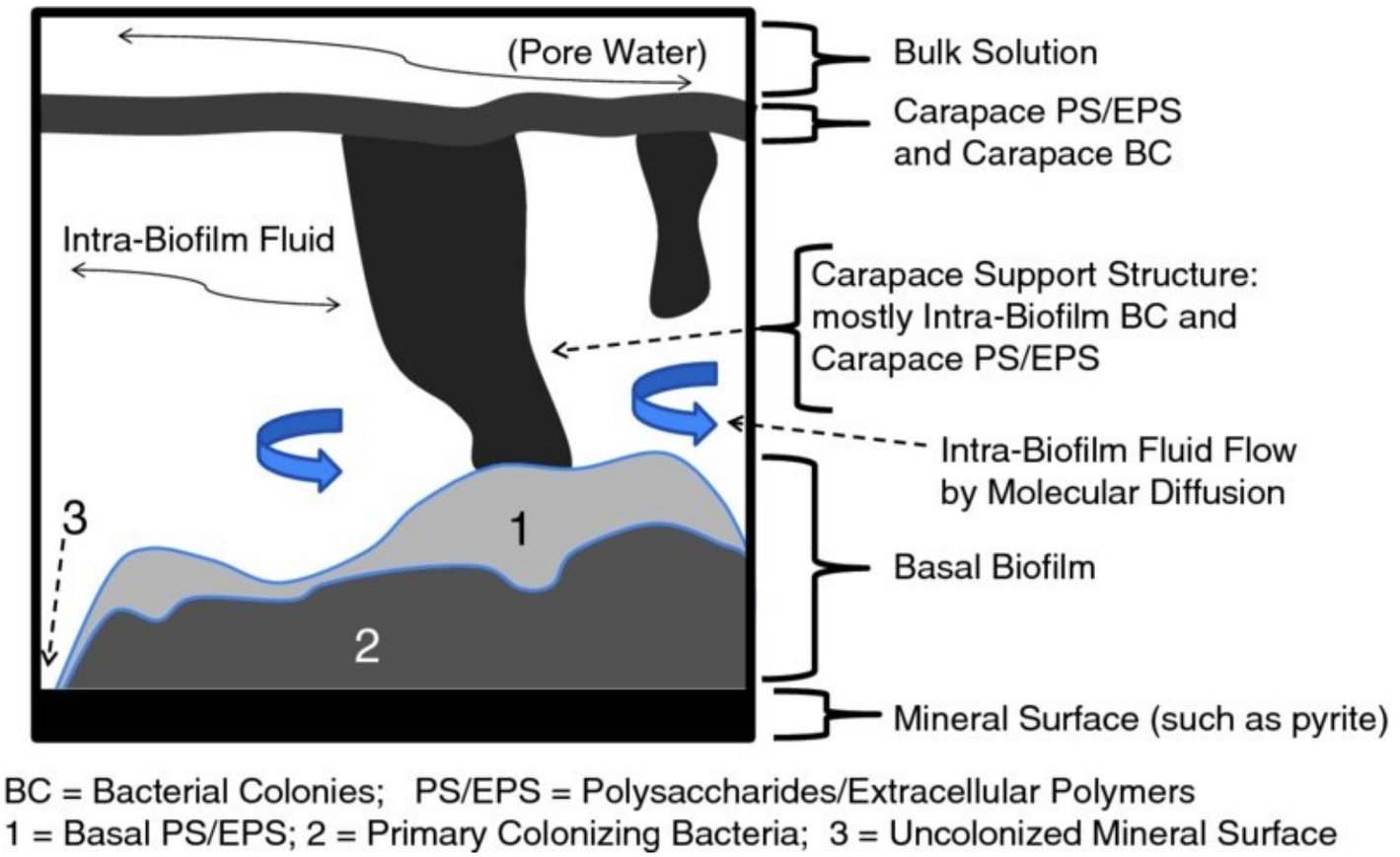


FIGURE 3.12 Biofilm morphology. BC, bacterial colonies; PS/EPS, polysaccharides/extracellular polymers; 1, basal PS/EPS; 2, primary colonizing bacteria; 3, uncolonized mineral surface. Not to scale. (Modified after Brydie et al., 2004, 2009, as seen in Newman et al., 2012.)

Geochemistry of Acid Drainage

Redox Reactions and Acid Drainage

Metals are characterized by their ability to lose electrons, thereby becoming positively charged ions. This process is termed *oxidation–reduction*, or *redox*. When a metal atom loses electrons, becoming more positive in the process, it is oxidized; when an atom or molecule gains electrons, becoming more negative, it is reduced (Neuman et al., 2009). This shift of electrons between atoms is a fundamental chemical process and provides the source of energy as part of the reaction. A common redox reaction is the oxidation of iron to form rust. In this chemical reaction, neutral elemental iron atoms Fe^0 lose three electrons, becoming Fe^{3+}, while elemental oxygen (O_2) sequesters the electrons as the terminal electron acceptor. The resulting molecule is iron oxide (Fe_2O_3), which contains iron with a valence state of 3 + and oxygen with a valence of 2−. Other metals can be oxidized when exposed to oxygen, resulting in positive ions that are often soluble in aquatic environments (Pagenkopf et al., 1974). A simple redox example uses two half-reactions with electron transfers:

$$\tfrac{1}{2}O_2 + 2e^- + 2H^+ \rightleftharpoons H_2O \quad \text{reduction half-reaction} \tag{3.1}$$

$$2Fe^{2+} \rightleftharpoons 2Fe^{3+} + 2e^- \quad \text{oxidation half-reaction} \tag{3.2}$$

The complete redox reaction is

$$\tfrac{1}{2}O_2 + 2H^+ + 2Fe^{2+} = 2Fe^{3+} + H_2O \quad (3.3)$$

Relationships among pH, oxidation–reduction potential or redox (Eh), and metal mobility are important in the study of acid generation and acid drainage. The oxidation–reduction potential of groundwater is a measure of electron activity and an indicator of the relative tendency of a biogeochemical system to accept or transfer electrons. In a highly oxidizing environment, the activity of electrons is low, but in a highly reducing environment, the activity of electrons is high. A detailed description of electron activity, the driving force of a redox reaction, and the oxidation–reduction potential is provided by Suthersan (2001).

Valence Electrons of Metals

Valence electrons of metals, those in the outermost orbital shells, determine how metal atoms lose, gain, and share these electrons with other elements. Valence electrons define four basic metal properties that influence behavior: electronegativity, oxidation state, ionic radius, and ionic potential. *Electronegativity* is the tendency of an atom to lose or gain electrons in the outer orbits. Elements with high electronegativity have a tendency to gain electrons; those with low electronegativity easily lose electrons. Most metals associated with acid drainage have low electronegativity and are therefore easily ionized into a positively charged form. Electronegativity therefore dictates the type of chemical reactions and chemical bonds that certain metals will form. *Oxidation state* is the charge that an atom has when electrons are counted and determines how electrons are allocated between atoms in oxidation–reduction reactions. Ionic radii relate to the size and shape of an elemental atom and are related to the oxidation state. Several metals (e.g., iron and copper) can exist in different oxidation states and can therefore take part in multiple redox reactions. *Ionic potential* is a measure of the ratio of oxidation number to ionic radius. Elements with similar ratios can sometimes substitute for each other in biological systems. Ionic potential partially explains how elements that seem chemically different can act similarly in the environment (Neuman et al., 2009). For example, the anions phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) are similar in chemical structure, and organisms can assimilate arsenic by using an active transport system normally used in phosphate transport (Eisler, 1988).

Measuring Redox Conditions

Eh is defined as the voltage reading from the liquid versus the standard hydrogen electrode (SHE) reading measured in millivolts, with temperature adjustments. Eh is measured almost exclusively in the laboratory and generally is not practical for field applications. A much less specific term is oxidation–reduction potential (ORP), in which the measurement of electron activity is also in millivolts. ORP can be made relative to any practical reference electrode, including Ag/AgCl, calomel, or SHE. Most field meters available will measure ORP in water rather than Eh.

Redox conditions greatly influence acid mine drainage processes. However, trying to measure apparent redox potential in the field is problematic, as noted by Morris and Stumm (1967), Whitfield (1974), Lindberg and Runnels (1984), Walton-Day et al. (1990), and Westall (2000). Conflicting redox measurements are common in the field, especially when dissolved oxygen and ORP readings suggest low dissolved oxygen (DO) levels. At these levels, colorimetric Fe(total) and Fe^{2+} kits may suggest reducing conditions predominate, whereas the DO and ORP measurements from the field meters suggest that aerobic environments are present. As noted by Westall (2000), instead of focusing on Eh or ORP field measurements for acid drainage projects, it is more accurate to evaluate the redox transformations taking place under a certain set of environmental conditions at a particular acid drainage site. This includes the

examination and recognition of the sets of conditions (e.g., major oxidant and reductant species, major metal ions, trace elements, and selected isotopes) that are redox indicators of specific geochemical processes taking place at the rock–water interface.

A detailed hydrogeochemistry study of the soluble iron compounds associated with acid drainage entering stream waters in Shasta County, California was performed by Nordstrom (1979). The complexity of the geochemistry of acid drainage from this study provides insight into the equilibrium transformations of iron during the oxidative weathering of iron sulfide ores. Over 60 water samples were collected along 14 km of stream waters in the metal mining area. The stream water samples analyzed varied in location and geochemical characteristics and covered a range of pH, redox state, total iron concentration, temperature, and ionic strength. The analytical results for the sample results were processed with the computerized chemical model WATEQ2 so that activities of free ions and complexes and saturation indices could be determined. The results as reported by Nordstrom (1979) demonstrated that the Eh values measured agreed quite well with the values calculated from the ferrous/ferric activity ratio. The water contained a large variety of iron compounds, and the dominant complexes in acid mine waters were FeS_4^0, $FeSO_4^+$, $Fe(SO_4)_2^-$, $Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$, and $Fe(OH)_2^+$. It was noted that acid mine waters low in pH (1 to 2) and high in reduced iron approach saturation with respect to melanterite (a hydrous ferrous iron sulfate with the composition of $FeSO_4 \cdot 7H_2O$), whereas progressive downstream oxidation and dilution (pH 2 to 3.5) of these waters forced the stream waters to become saturated with respect to amorphous iron hydroxide. For these two minerals, the field observations match the saturation calculations very well. However, all of the waters show supersaturation with respect to jarosite (with ferric iron), regardless of the presence or absence of jarosite in the stream waters. These results suggest a strong kinetic hindrance to the precipitation of jarosite (Nordstrom, 1979). This stream study demonstrates the level of analysis that is required to understand the detailed geochemistry associated with acid drainage projects.

Nordstrom (2000) noted the problem of trying to define redox conditions in several acid drainage examples of the same water sample, containing two or more of the following constituents: O_2, Fe^{2+}, Fe^{3+}, N_2, NO_3, NH_3, H_2S, SO_4, CH_4, CO_2, and H_2. Proper characterization of the aqueous geochemistry requires analyzing all the major ions, all the trace elements, redox species, and isotopes and performing appropriate laboratory Eh measurements and calculations. This geochemistry approach allows for better site-specific understanding of redox conditions. Tables 3.1to 3.3 show the types of detailed field measurements useful for all acid drainage studies, regardless of environmental setting.

TABLE 3.1 Sampling Parameters for Acid Drainage Studies

Parameter	Comments
Field measurements	
Temperature	Must be done in the field; downhole (monitoring wells) preferred
pH	Must be done in the field; robust; easily measured; flow cell recommended
Eh	Must be done in the field; variable; more standard checks recommended; flow cell recommended
Dissolved oxygen	Must be done in the field; variable; accuracy of probes limited at less than 1 mg/L
Turbidity	Must be done in the field
Specific conductance	Recommended for the field
Alkalinity	Recommended for the field
Redox indicators	S^{2-}, H_2
Laboratory analyses: water	
Major cations	Ca, Mg, Na, and K
Major anions	HCO_3/CO_3, Cl, SO_4, NO_3/NO_2
Redox indicators	Mn, Fe, S^{2-}, As(III)/As(V), CH_4, DOC
Minor/trace constituents	Al, Si, PO_4, Br, F
Metals of potential concern	As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Tl, Zn

Source: After Puls and Deutsch (2000).

TABLE 3.2 Site-Specific Redox Field Measurements for Acid Drainage Studies

Core Parameter:	**Site-Specific Parameters**	
Groundwater	***Groundwater***	***Solid-Phase***
Temperature	Dissolved inorganic carbon	Oxidizing capacity
Eh, pH, alkalinity	Total dissolved solids	Reducing capacity
Turbidity	Fluoride	Neutralization capacity
Total and ferrous iron	Hydrogen	Adsorption capacity
Dissolved oxygen	Methane	Cation-exchange capacity
Specific conductance	Sulfide	Acid generation capacity
Dissolved organic carbon	Priority metal contaminants (As, Cd, Cr, Cu, Hg, etc.)	Total metal(s) concentration
Major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, S^{2-}, SO_4^{2-}, NO_{3-}, ammonium, phosphate)		Iron/aluminum extraction
Aluminum, silica, manganese		Mineralogy (x-ray diffraction)
		Total organic carbon
		Sulfur extraction

Source: After Puls and Deutsch (2000).

Table 3.3 Redox Measurements and Methods of Measuring

Parameter	Common Field Methods	Standards for Performance Assessments	References
Oxidation–reduction potential	Combination platinum electrode with Ag/AgCl reference electrode; KCl filling solution	Zobell's solution; Light's solution	Langmuir (1971); Nordstrom (1977); Standard Methods for the Examination of Water and Wastewater (1999)
Dissolved oxygen	Membrane-covered electrode; colorimetric (high range, indigo carmine); colorimetric (low range, rhodazine D); modified Winkler titration	Air-saturated water	Hitchman (1978); Gilbert et al. (1982); White et al. (1990); Standard Methods for the Examination of Water and Wastewater (1999)
Iron speciation	Ferrous iron colorimetric indicators (1,10-phenanthroline; ferrozine)	Prepared ferrous solutions	Tamura et al. (1974); Stookey (1970)
Sulfur speciation	Sulfate (turbidimetric); sulfide (methylene blue colorimetric method)	Prepared sulfate and sulfide solutions	Standard Methods for the Examination of Water and Wastewater (1999); Cline (1969)
Nitrogen speciation	Nitrate + nitrite (cadmium reduction); ammonia (Nessler method; salicylate method)	Prepared nitrate, nitrite, or ammonia solutions	Standard Methods for the Examination of Water and Wastewater (1999)
Alkalinity	Acid titration	Prepared bicarbonate or carbonate solutions	Standard Methods for the Examination of Water and Wastewater (1999)

Source: After Wilkin and Ptacek (2000).

Mobility, leachability, and bioavailability of metals are affected by pH. Under low-pH conditions and positive oxidation conditions wherein the Eh measured in the laboratory or the ORP measured in the field is a high positive number, acidification is favored. Acid conditions tend to make most metals more mobile and bioavailable, as indicated on the right in Figure 3.6. Under anaerobic conditions, metals frequently will precipitate or stay insoluble as sulfides. Metals tend to precipitate as oxides and hydroxides under elevated pH/positive Eh conditions. Negative Eh values indicate a reducing environment, most metals form sulfides under these conditions, and mobility is limited (Neuman et al., 2009).

Geochemical Environment of Acid Mine Drainage

Environments with extremely low pH values are not that common on Earth. One environment with low pH is associated with volcanic activity such as hot sulfur springs and mud pots. Another low-pH environment is associated with naturally occurring chemoautotrophic microbial communities that thrive in a pH value

below 3. These microbes oxidize sulfide, elemental sulfur, and other reduced sulfur compounds, creating sulfuric acid, which acidifies the medium. Another source of low-pH environments comes from fermentations of some carbon substrates, such as lactic acid, in an oxygen-free environment that may also decrease the pH of soils and aquatic ecosystems (Rainey and Oren, 2006).

Acidic drainage is found around the world both as a result of naturally occurring processes and anthropogenic activities associated with land disturbances, such as mining, construction of highways, airports, tunnels, dams, and land development where acid-forming minerals are exposed. Once sulfuric acid is generated, the acidic conditions cause reduced metals in the soils or rocks to become soluble, which can lead to significant impairment of water quality when acidic and metal-laden discharges enter surface water bodies or groundwater. The pyrite exposure to the acidophilic microbial communities, in combination with oxygen in the atmosphere or dissolved in water, leads to sulfide oxidation and the production of extremely acidic drainages. The acidic drainages are frequently enriched with Fe, Mn, Al, Cu, Zn, Cd, Pb, and As and the SO_4 anion (Evangelou, 1995, 1998).

Sulfur accumulates by formation of sulfate and sulfide minerals and with the burial of biomass, which creates anaerobic conditions as the carbon substrates are allowed to ferment and degrade by anaerobic oxidation. The iron sulfides are released in the case of acid drainage, ultimately generating sulfuric acid by oxidation or dissolution of sulfur-bearing minerals. The key to preventing acid generation related to surface disruption is managing the disequilibrium between the various sulfur compounds, the indigenous iron- and sulfur-oxidizing microorganisms, and the associated changes to redox, pH, and other geochemical conditions that cause environmental instability. The ecology and biodiversity of the microbial communities are described in detail by Baker and Banfield (2003) and Baker et al. (2004).

The reaction of pyrite with oxygen and water produces a solution of iron(II) sulfate and sulfuric acid. Fe^{2+} can be oxidized further to Fe^{3+}, producing additional acidity. Iron- and sulfur-oxidizing bacteria are known to catalyze these reactions at low pH, thereby increasing the rate of reaction by several orders of magnitude (Nordstrom and Southam, 1997). In undisturbed natural systems, this oxidation process occurs at slow rates over geological time periods. When pyrite is exposed to oxygen and water, it is oxidized, resulting in hydrogen-ion release, creating acidity, sulfate ions, and soluble metal ions, as shown in reaction (3.4). The acidity of water is typically expressed as pH or the logarithmic concentration of hydrogen-ion concentration in water such that a pH of 6 has 10 times the hydrogen-ion content of neutral pH 7 water (Jennings et al., 2008). Detailed metal-leaching characteristics of acid rock drainage have been known for decades and are well documented (MEND, 2005). The actual pyrite oxidation proceeds in various stages, regardless of whether the pyrite oxidation is associated with coal seams, hardrock mining, or acid sulfate soils. The chemical equations from Singer and Stumm (1970), Evangelou (1995, 1998), Stumm and Morgan (1996), Thomas et al. (2003), and Jennings et al. (2008) approximate the general pyrite oxidation process, regardless of whether the setting relates to a coal mine or a hardrock mine, or to acid sulfate soils. Reactions (3.4) to (3.8) show the overall sequence of mineral reactions important in aqueous pyrite oxidation and are based on Jennings et al. (2008). These reactions represent the chemical stoichiometry with the elements, compounds, and ions listed. They do not show the important microbial input to the rate of reaction, which is significant.

$$2FeS_{2(s)} + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO^{2-}_{4(aq)} + 4H^{+}_{(aq)} \tag{3.4}$$

$$4Fe^{2+}_{(aq)} + O_2 + 4H^{+}_{(aq)} \rightarrow 4Fe3^{3+}_{(aq)} + 2H_2O \tag{3.5}$$

$$2Fe^{3+} + 6H_2O \rightleftharpoons 2Fe(OH)_{3(s)} + 6H^{+}_{(aq)} \tag{3.6}$$

$$14Fe^{3+} + FeS_{2(s)} + 8H_2O \rightarrow 15Fe^{2+}_{(aq)} + 2SO_4^{2-} + 16H^+_{(aq)} \quad (3.7)$$

$$FeS_{2(s)} + 7Fe_2(SO_4)_{3(aq)} + 8H_2O \rightarrow 15FeSO_{4(aq)} + 8H_2SO_4 \quad (3.8)$$

Reaction (3.4) shows the overall acid generation equation oxidizing pyrite (FeS_2)-forming hydrogen ions, which later combine with the sulfate (SO_4^{2-}) to form sulfuric acid (H_2SO_4). Reaction (3.5) shows that further oxidation of Fe^{2+} (ferrous iron) to Fe^{3+} (ferric iron) occurs when sufficient oxygen is dissolved in water or when the water is exposed to sufficient atmospheric oxygen. The ferric iron can precipitate as ferric hydroxide [$Fe(OH)_3$], a reddish-orange to yellow precipitate seen in acid rock drainage waters. At a low pH (<4.5), Fe^{3+} oxidizes pyrite much more rapidly than O_2 and more rapidly than O_2 oxidizes Fe^{2+} (Nordstrom, 1982). Consequently, reaction (3.5) is known to be the rate-limiting step in pyrite oxidation. Iron-oxidizing bacteria can accelerate the rate of Fe^{2+} oxidation by a factor of 10^6 (Singer and Stumm, 1970). As sulfuric acid is produced, it can be neutralized through a reaction with naturally occurring adjacent soil carbonates or shell fragments, or by displacing exchangeable cations. Excess acidity then reacts with rock or soil minerals, releasing major constituents such as potassium, magnesium, aluminum, and silicon, as well as trace elements such as arsenic, copper, cadmium, chromium, nickel, and zinc.

Reaction (3.6) is a readily reversible dissolution–precipitation reaction, taking place at pH values as low as 3, which serves as a source or sink of solution Fe^{3+}. It is the major step in the release of the acidic sulfate (sulfuric acid) to the environment (Evangeolu, 1998). The ferric iron in (3.6) can be hydrolyzed and precipitate out of the solution as ferric hydroxide [$Fe(OH)_3$] with some hydrogen ions. The ferric iron can also react with additional pyrite (FeS_2) to produce excess H^+ ions to lower pH and increase acidity as shown in (3.7). Reaction (3.8) shows the increasing production of sulfuric acid as unreacted pyrite is being oxidized in water. Further, microbial communities attached to iron sulfide mineral grain surfaces catalyze the oxidation of pyrite and the generation of sulfuric acid.

Origin of Pyrite and Sulfur in Rocks and Soils

Pyrite, also called *iron pyrite*, is the most common of the sulfide minerals, with a formula of FeS_2. Geologically, pyrite is found in a variety of settings. Oceanic volcanic hydrothermal vents, including “black smokers” on the seafloor of tectonically active regions, are a source of pyrite formation. Black smokers are also an important habitat of sulfide-oxidizing bacteria. According to Chapelle (1993), the characteristic black clouds of sulfides that emanate from hydrothermal seafloor vents are subject to rapid oxidation by means of oxygen present in the seawater. When the oxygen available in the local seawater is insufficient to meet the oxidation demand for the mass of sulfides being emitted, metal sulfide deposits can collect. This also takes place within the seawater subsurface of the seafloor in the hydrothermal circulation systems driven by infiltrating seawater, where the oxygen dissolved in the circulating water is limited as well. Some of those ancient marine volcanic deposits have been uplifted and are now located in continental mining districts.

Pyrite is usually found associated with other sulfides or oxides in quartz veins in igneous and metamorphic rocks. In addition, pyrite is found in sedimentary rocks, particularly in reducing environments rich in organic materials, such as coal beds, marine deltas, and wetlands. Pyrite is also a replacement mineral in fossils.

Pyrite has a metallic luster and a pale-to-normal brass-yellow hue. Despite the common name “fool's gold,” pyrite is sometimes associated with gold. Gold and arsenic occur as a coupled substitution in the

pyrite structure, and auriferous pyrite is an ore of gold. Hardrock gold mines are frequently located in areas that contain high concentrations of sulfide minerals, and primary among those minerals is pyrite. Acid drainage chemistry is not limited to sulfide deposits associated with hardrock mines, as the originally reducing sedimentary environments associated with coal deposition were also favorable to the deposition and preservation of pyrite in nearshore environments.

Coal Depositional Environment

Paleoenvironments under which coal seams formed can be characterized into three general categories: marine, freshwater, and brackish. Studies of Pennsylvanian age coal-bearing rocks have shown that the paleoenvironment can be used to broadly define acid drainage potential (Hornberger et al., 1981; Brady et al., 1988; Skousen et al., 1998). Rocks formed under brackish-water conditions are generally most prone to acid production. Freshwater systems usually produce nonacid mine water. Marine depositional systems produce variable drainage quality. In some coal measures, the paleoenvironment varies laterally and vertically within a single mine site and is a controlling factor in the inherent distribution of pyrite and carbonates. Due to this variability, acid drainage potential may also vary significantly within the same coal mine.

Acid Sulfate Soils

Although the pyrite-rich rock wastes from hardrock mines and coal mines generate acid drainage, soils and sediments that contain pyrite and other iron sulfide minerals create acid drainage in a completely different geological setting and possibly with different trace metals, but the overall geochemistry is identical. Throughout the world, uncemented or weakly cemented soils and sediments frequently reflect the accumulation of mineral and organic particles found above the bedrock source material in a variety of coastline areas and in former marine and estuarine geologic settings. These soils and sediments produce significant acid drainage. Acid sulfate soils are soils and marine sediments that contain pyrite and other iron sulfides. They are commonly found in coastal lowlands, estuaries, floodplains, wetlands, uplifted marine terraces, and mangrove environments.

Acid sulfate soils contain elevated iron sulfides, most notably, pyrite. Acid sulfate soils are strongly acidic ($pH < 3.5$), creating land development and agricultural challenges in many countries. When acid sulfate soils are exposed to oxygen through drainage or disturbance, the sulfuric acid is generated where it can be flushed by rainfall or high groundwater into nearby waterways, killing fish and other aquatic organisms and vegetation. Land uses on the acid sulfate soils include canal and residential estates, marinas, aquaculture, road construction, sand and gravel extraction, and golf courses (Department of Environment and Resource Management, 2009).

Regardless of the source of the iron sulfide minerals (hardrock mining, coal mining, land development, natural acid rock drainage, or acid sulfate soils), if the iron sulfide minerals can be isolated and prevented from being exposed to oxygen and water, acid generation will be minimal. Avoidance or minimizing the disturbance of the iron sulfide minerals is the lowest-cost strategy for the prevention of acid drainage. Unfortunately, this approach may not be possible at many locations, such as orphan mine sites, where disturbance has occurred in the distant past. Once the microbial initiated process starts, oxidation of sulfide minerals will occur with the production of sulfuric acid, and stopping the process is unlikely, whether the location is a hardrock mine site, a coal mine site, or a marina project in acid sulfate soils.

Geochemical Processing and Sulfur in Rocks, Sediments, and Soils

Sulfur can occur in many forms in rocks, including sedimentary, igneous, and metamorphic. Sulfur and sulfur compounds can also occur in unlithified sediments or in soils. Elemental sulfur is found in many different environmental and geologic settings. Sulfur also occurs as a compound, readily bonding with iron, sodium, potassium, magnesium, calcium, and aluminum, as well as other elements. Soluble sulfates include sodium sulfate, potassium sulfate, and magnesium sulfate. Moderately soluble sulfates such as gypsum ($CaSO_4 \cdot 2H_2O$) are commonly mixed with other evaporite deposits. Some sulfate minerals have low solubility and are frequently associated with shallow acid sulfate soils such as jarosite [$KFe_3(SO_4)_2(OH)_6$], natrojarosite [$NaFe_3(SO_4)_2(OH)_6$], and other iron or aluminum sulfates. Sulfur is commonly found as a disulfide mineral such as pyrite or marcasite (FeS_2). Monosulfide minerals such as greigite (Fe_3S_4) and mackinawite, with an approximate chemical formula of FeS, and various other iron monosulfides are also found in rocks, sediments, and soils. Although elemental sulfur and sulfur compounds are found in relative abundance in nature, not all the forms of sulfur in rocks, sediments, and soils produce sulfuric acid. For example, gypsum contains completely oxidized sulfate and does not produce acid. Those sulfur compounds that do produce acid can produce differing amounts per mole of sulfur present, as pyrite produces different amounts of acid compared to jarosite (Ahern et al., 2004).

Sulfide Minerals

Pyrite is the most abundant sulfide mineral; it is widespread in ore deposits and common in many sedimentary, metamorphic, and igneous rocks. It exhibits a range of interesting structural characteristics, such as penetration twins, epitaxial inter- and overgrowths with its polymorph marcasite, and the occurrence of a variety of morphological types (Tokody, 1952; Donnay et al., 1977; Bonev et al., 1985). Pyrite and marcasite are polymorphs. Fe atoms are coordinated octahedrally in both structures. The octahedral share corners in pyrite, whereas in marcasite they share edges (Buerger, 1931; Dodony et al., 1996). Although iron sulfides are predominately pyrite and marcasite (FeS_2), other metals may be combined with sulfide in the form of chalcopyrite ($CuFeS_2$), covellite (CuS), and arsenopyrite (FeAsS).

Sulfur Associated with Metal Ores

Metal ores frequently have elemental sulfur or sulfur compounds associated with the ore body. Table 3.4 highlights some of the important metal sulfides that occur in mining regions as documented by Plumlee et al. (1999). Of the various sulfide compounds, the predominant acid producers are pyrite and marcasite. Table 3.5shows some important metal sulfides that occur in coal mining as well as metal ore mining regions. Authigenic minerals are formed in place and include some sulfate minerals that were deposited from acid solutions. A summary of sulfate mineral solubility is shown in Table 3.6. Calcium sulfate and silver sulfate are moderately (2,200 mg/L SO_4 for gypsum) soluble. Barium sulfate, lead(II) sulfate, and strontium sulfate are insoluble.

TABLE 3.4 Mineralization Types, Examples, and Associated Rock Types

Mineralization Types	Examples	Associated Rock Types
Volcanogenic massive sulfide	Iron Mountain, CA; Blackbird mine, ID	Volcanic: basaltic (Cyprus type), rhyoliticandesitic (Kuroko type);

deposits		sedimentary rock such as turbidites and black shales (Besshi type)
High sulfidation epithermal (quartz alunite epithermal) deposits	Summitville, CO; Red Mountain Pass, CO; Goldfield and Paradise Peak, NV; Mt. Macintosh, BC; Julcani, Peru	Silicic volcanic or intrusive rocks (e.g., quartz latite)
Porphyry Cu and Cu–Mo deposits	Globe, AZ; Mt. Washington, BC; Alamosa, CO	Altered, intermediate-composition intrusive rocks
Cordilleran lode deposits	Butte, MT; Magma, AZ; Quiruvilca, Peru	Altered, intermediate-composition intrusive rocks
Climax-type porphyry Mo deposits	Climax, Henderson, Mt. Emmons, CO	Silica- and uranium-rich granitic or rhyolitic intrusions
Polymetallic vein deposits and adularia–sericite epithermal vein deposits	Central City, CO (polymetallic vein); Creede and Bonanza, CO; Comstock, NV; Sado, Japan (adularia–sericite)	Igneous intrusions
Hot-spring Au–Ag and Hg deposits	Leviathan, Sulphur Bank, and McLaughlin, CA; Round Mountain, NV	Epithermal and vein deposits; volcanic rocks
Skarn and polymetallic replacement deposits	Leadville, Gilman, and Rico, CO; New World, MT; Park City and Tintic, UT; skarn deposits associated with porphyry-Mo, -Cu–Mo, and porphyry-Cu deposits, Yerington, NV; Chino, NM	Outermost portions of intrusions or in sediments adjacent to the intrusions
Stratiform shale-hosted deposits	Red Dog, Lik, and Drenchwater, AK; Sullivan, BC; Mt. Isa and Broken Hill, Australia	Black shale and chert-bearing host rocks
Mississippi Valley–type deposits	Old Lead Belt, Viburnum Trend in Missouri, Tri-State (Missouri, Kansas, and Oklahoma), Northern Arkansas, Upper Mississippi (Wisconsin), and Central Tennessee districts	Dolostones, limestones, sandstones in sedimentary basins
Magmatic sulfide deposits	Sudbury Complex, Ontario; Duluth Complex, MN; Stillwater Complex, MT; Bushveld Complex, South Africa	Layered mafic intrusions; ultramafic volcanic rocks or ultramafic accumulations
Banded-iron formation deposits	Superior-type deposits, Mesabi Iron Range, MN; Marquette Iron Range, MI	Chemical sediments in which iron oxides, carbonates, silicates, or sulfides are finely interlaminated or interbedded with chert or jasper
Low-sulfide gold–quartz vein deposits	Juneau Gold Belt and Fairbanks, AK; Mother Lode, CA	In quartz veins in medium-grade greenstone metamorphic rocks
Alkalic Au–Ag–	Cripple Creek, CO; Boulder County, CO; Ortiz,	Diatremes or breccia pipes in

Te vein deposits	NM; Zortman and Landusky, MT	alkalic igneous intrusive complexes

Source: Plumlee et al. (1999).

TABLE 3.5 Some Important Metal Sulfides That Occur in Mining Regions

Chemical Formula	Mineral Name	Solubility in Water
FeS_2	Pyrite	Insoluble
FeS_2	Marcasite	Insoluble
FexSx	Pyrrhotite	Insoluble
Cu_2S	Chalcocite	Insoluble
CuS	Covelite	Insoluble
$CuFeS_2$	Chalcopyrite	Insoluble
MoS_2	Molybdenite	Insoluble
NiS	Millerite	Insoluble
PbS	Galena	Insoluble
ZnS	Sphalerite	Insoluble
FeAsS	Arsenopyrite	Insoluble

Source: After Skousen et al. (1998).

TABLE 3.6 Some Highly Soluble Metal Sulfates

Chemical Formula	Mineral Name	Solubility in Water
$KAl_3(SO_4)_2(OH)_6$	Alunite	Soluble
$Cu_3SO_4(OH)_4$	Antlerite	Soluble
$Al_4SO_4(OH)_{10}$	Basaluminite	Soluble
$Cu_4SO_4(OH)_6$	Brochantite	Soluble
$KFe_3(SO_4)_2(OH)_6$	Jarosite	Soluble
$AlSO_4OH$	Jurbanite	Soluble
$FeSO_4 \cdot 7H_2O$	Melanterite	Soluble

Sulfur Associated with Coal

Sulfur in coal and rocks associated with coal mines can occur as organic sulfur, sulfate sulfur, and pyritic sulfur. Based on the research of Skousen et al. (1998), some sulfur in coal appears to have been introduced after the peat had been converted to coal, as is evidenced by pyrite coatings on vertical fracture surfaces, called *cleat*, in the coal seam. Much of the pyrite present in rocks and overburdens of coal mines occurs as very small crystalline grains mixed intimately in sandstones and shales (Temple and Koehler, 1954). The occurrence of fine pyrite grains in and near coal seams is evidence that the iron sulfides were deposited in a reducing environment and that the sediments were buried and cemented prior

to exposure to oxygen, water, and iron-oxidizing bacteria that would have dissolved the pyrite, creating sulfuric acid in the process.

The origin of sulfur in large concretions, nodules, lenses, bands, and fillings in porous layers of coal is less well understood (U.S. Geological Survey, 1968). Organic sulfur is believed to be complexed and combined with organic constituents of coal and bound organically within the coal. This form of sulfur is found in appreciable quantities only in coal beds and in other carbonaceous rocks. Generally, the organic sulfur component is not chemically reactive and has little or no effect on acid-producing potential.

Sulfate sulfur is usually found in only minor quantities in fresh coal and other undisturbed pyrite-containing rocks, and is commonly the result of weathering and recent oxidation of sulfide sulfur. Some sulfate minerals, such as jarosite [$KFe_3(SO_4)_2(OH)_6$], can dissolve in acid solutions in coals and hardrock metal deposits. The highly acid-soluble sulfate jarosite is also commonly found in near-surface coastal environments and is common in acid sulfate soils.

Pyritic or sulfide sulfur is the dominant form of sulfur in the majority of coal and associated rocks. It is the sulfur form of greatest concern. Of all the sulfide minerals that may be present, Fe disulfides predominate and are the major acid producers. Accordingly, the maximum potential acidity of a fresh overburden sample correlates closely with the pyritic sulfur content. Studies have shown that variations in total sulfur contents of overburden samples reflect similar variations in pyritic sulfur content. Several types of pyritic sulfur are known based on physical appearance, and they are classed into six main groups: (1) primary massive, (2) plant replacement pyrite, (3) primary euhedral pyrite, (4) secondary cleat (joint) coats, (5) mossy pitted pyrite, and (6) framboidal pyrite. Caruccio et al. (1988) have reviewed extensively the various forms, morphologies, and reactivity of pyritic materials.

The chemical reactions for pyrite oxidation show that a material containing 1% sulfur, all as pyrite, would yield upon complete oxidation of the iron sulfide an amount of sulfuric acid that requires 31.25 mg of $CaCO_3$ to neutralize 1000 mg of iron sulfide. This answer can also be stated as tons of neutralizing agent per 1000 tons of the material (Sobek et al., 1978). When sulfur in the rock is exclusively pyrite, the total sulfur content of the rock quantifies the acid-producing potential accurately if it were all to react. When organic or sulfate sulfur is present in significant amounts in partially weathered rocks, total sulfur measurements overestimate the amount of acid that will be formed upon oxidation. Therefore, correction for sulfates and organic sulfur naturally present in some overburdens or resulting from partial weathering of pyritic materials may be necessary to increase accuracy in predicting the acid-producing potential of materials containing mixed sulfur species.

Although large variations in sulfur content do exist between sites, a typical example of the concentrations of percent total sulfur in typical shallow Carboniferous bituminous coal seams comes from the work of Kleinmann and Rastogi (1994). In one case from the summit of Cover Hill approximately 3 miles northwest of Berlin, Pennsylvania, the coal itself was 2 ft thick, with a total sulfur content of 3.670%. The underlying marine limestone was 3 ft thick with a total sulfur content of 1.070%. The 13 ft of dark gray marine shales overlying the Lower Bakerstown coal seam had a range of total sulfur of 0.647 to 1.180%, with an average total sulfur of 0.81% over the 13 ft of marine sediments.

Microbiological Biogeochemistry of Acid Mine Drainage

Although abundant on Earth, microorganisms, or microbes, are too small to see without a microscope, yet they live everywhere: in air, soil, rock, and water. These microscopic organisms are found in both plants and animals. Moving ever smaller, a scanning electron microscope image shows microbial colonies of a

major sulfur-oxidizing bacterium, *Acidithiobacillus ferrooxidans*, on pyrite in Figure 3.13.

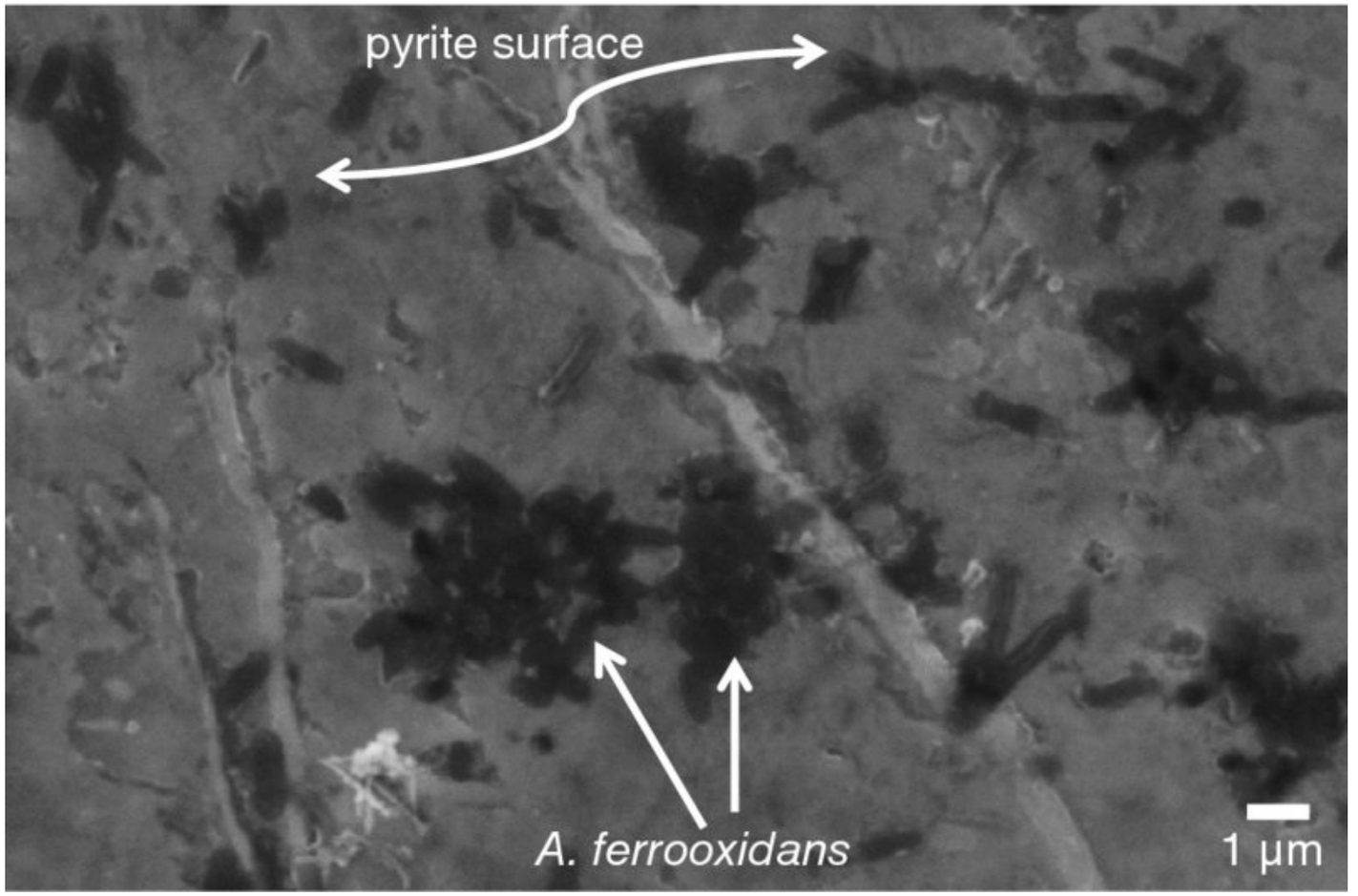


FIGURE 3.13 Scanning electron micrograph of a pyrite surface after 30 days of colonization with *A. ferrooxidans* (dark rods). (Courtesy of R. Mielke and G. Southam; used by permission.)

Since microbes are far too small to be seen with the naked eye, microscopes have been used to view microbes since 1676, when a Dutch scientist, Anton von Leeuwenhoek, first observed microbes collected from lake water and bacteria scraped from his teeth. More advanced optical or light microscopes have subsequently been used for viewing microbes. For better identification, since many microbes are colorless and transparent, stains and dyes began to be used in 1856 to stain microbes. Genetic testing and other identification techniques are used routinely today to identify microbial populations for acid mine drainage studies, as well as studies related to bioleaching of metal resources and microbial-induced corrosion. Current microbiological methods available to evaluate indigenous microbial populations qualitatively and quantitatively can be summarized as follows:

- Quantitative polymerase chain reaction (PCR, DNA based)
- Biochemical methods (DNA composition and kinetic assays)
- Metabolic assays
- Lipid analysis (quinones, phospholipids, and methyl esters)
- Microbiological methods (metabolic assays, cell counts, and flow cytometry and cell sorting)

Variations of technique within each of these methodologies can assess population counts in water, on soils, or in biofilms, and can evaluate specific metabolic pathways and species that are present and

active. Bear in mind that sampling technique is important, with many options, ranging from discrete sampling to the placement of various types of probes in situ to collect populations over time. However, for a number of reasons, no single or combination of sampling techniques will capture all of the indigenous species present. Microbial consortia can also vary significantly at a location over distances of a few meters, even in uniform biogeochemical environments. The tools described above are very helpful, but they may not tell the complete story, so evaluation of other indicative indicators, such as the biogeochemistry, should be part of the assessment.

Genetic Sequences

Fluorescent in situ hybridization has been used to find the position of genes and to detect specific RNA or DNA sequences in microbes and cells. Electron microscopes were first built in 1931. The transmission electron microscope produces black-and-white images by passing electrons through an object such as a microbe; some of the electrons are absorbed by the object while other transmitted electrons are captured on a specific photographic plate to preserve the image. The scanning electron microscope was developed around 1935; this tool captures a three-dimensional image of an object by scanning the surface with electrons (Noel, 2012). Recent advances in microbial imaging by devices such as the confocal scanning laser microscope and cryoelectron microscope have allowed for more accurate size determination, identification of particular microbial community architecture, and high-resolution three-dimensional images of ultrasmall microbes. Understanding the size of acidophilic microorganisms is important to better evaluate the spatial arrangement of the microbes and the mineral grain surfaces, transport mechanisms in liquids and gases at that scale, and the organizational structure of microbial communities. Optimization of environmental conditions for chemoautotrophic sulfur- and iron-oxidizing microbial communities is exploited by mining operations using bioleaching processes for the recovery of copper, gold, and other valuable metals.

Practical genetic testing for the identification of microbial populations was used at the Penn mine in California. This Cu–Zn mine was active from 1861 to 1953 and abandoned in the early 1960s. The Penn mine has acid drainage in the abandoned mine workings that has a pH value of 4. Like many abandoned mines with low pH values, this area does not have natural neutralizing agents such as carbonates. The mine sediments were analyzed for phospholipid fatty acids and denaturing gradient gel electrophoresis (DGGE). The details of the laboratory procedures have been described by Church et al. (2007). The DGGE gel image of 16S rDNA fragments from Penn mine sediments shows five labeled bands (Figure 3.14). Sequence identification of the five bands (A through E) compared the results with a similarity index of other known and identified sequences, allowing for accurate microbial identification of several species. In the Penn mine study (Church et al., 2007), the genetic data provided new evidence of microbial sulfate reduction, metal attenuation, and according to the authors, demonstrated to some degree the efficacy and processes for the remediation of natural acid generation at the Penn mine. These genetic techniques provide accurate identification of various microbial communities that would have been unavailable decades ago.

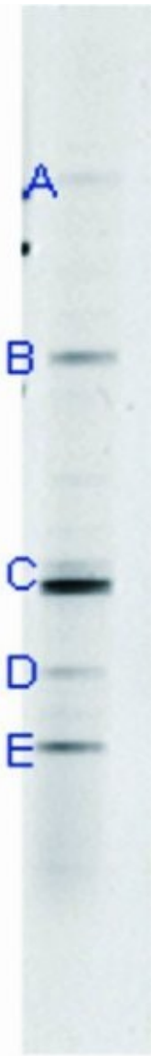


FIGURE 3.14 DGGE gel image of 16S rDNA fragments from Penn mine sediments with five bands labeled. (From Church et al., 2007.)

Microbial Genetic Studies

Microbes have been influencing Earth's history for about 4 billion years, transforming inorganic and organic compounds to meet their nutritional and energy requirements. On a global scale, microbes have been involved in all the major global-scale cycles, including carbon, sulfur, nitrogen, and oxygen. It is thought that the early environments on Earth were anoxic prior to the appearance of bacterial oxygenic photosynthesis (Baker and Banfield, 2003). The entire 20.9% of oxygen in Earth's atmosphere was probably produced by photosynthetic bacteria, such as *cyanobacteria*, over billions of years. These microbes acquire energy from the Sun and use carbon dioxide for cellular respiration, releasing oxygen as a waste product.

Using genetic studies, Woese and Fox (1977) and Siefert and Fox (1998) used single gene sequences to determine the phylogentic relatedness between many different organisms. Detailed descriptions of microbial properties, diversity, and genetic studies were given by Konhauser (2007) and Baker and Banfield (2003). The phylogenetic tree is based on genetic studies of 16S and ribosomal rRNA for prokaryotic organisms (bacteria and archaea), and for the eukayotes the equivalent but slightly larger molecule, 18S rRNA. For size, most bacteria and archaea have a diameter of between 500 nm and 2 μm with a volume between 1 and 3 μm^3 and a wet weight of about 10^{-12} g. Individual cells occur as rods

(bacilli), spheres (cocci), or helical shapes (spirilla or vibrio). Protists (such as algae and protozoans) and fungi are eukaryotes but are also microorganisms. Eukaryotes have a significantly more complex internal cellular structure and are typically larger than bacteria and archaea. Eukaryotes include multicellular life such as plants and animals. For size, eukarya are typically 5 to 100 μm; however, Konhauser (2007) notes that size variations do exist based on marine microbial discoveries over the past decade or so.

The sulfur-oxidizing bacteria can be subdivided into four main physiological groups: (1) acidophilic aerobic iron oxidizers associated primarily with acid drainage and oxidizing iron sulfide minerals, (2) neutrophilic aerobic iron oxidizers, (3) neutrophilic anaerobic (nitrate-dependent) iron oxidizers, and (4) anaerobic photosynthetic iron oxidizers. Some species (mostly acidophiles) can reduce ferric iron as well as oxidize ferrous iron, depending on prevailing environmental conditions.

The rRNA molecules (16S and 18S) have remained structurally and functionally conserved and are used to help identify organisms. All organisms now living on Earth have descended from the last universal common ancestor (LUCA). The phlogenetic tree (Figure 3.15), based on 16S and 18S rRNA sequence comparisons, show three domains of life (bacteria, archaea, and eukarya). The base of the phylogenetic tree is LUCA. In the phylogenetic tree, the bacteria and archaea are subdivided by representative phyla. Due to a general lack of agreement by taxonomists, the eukarya contain only familiar or common group names. A detailed phylogenetic tree based on the 16S and 18S rRNA sequence for microorganisms identified in highly acidic waters shows a variety of microbes associated with acidic conditions (Figure 3.16). Chemical reactions are shown in a simplified schematic of electron transport chain and the generation of a proton motive force in acidophilic iron-oxidizing bacteria in the presence of pyrite (Figure 3.17). Detailed discussions and diagrams of electron transport processes in acidophilic microbes are available (Ingledew, 1977; Apel et al., 1980; Baker-Austin and Dopson, 2007; Konhauser, 2007; Knoll et al., 2012).

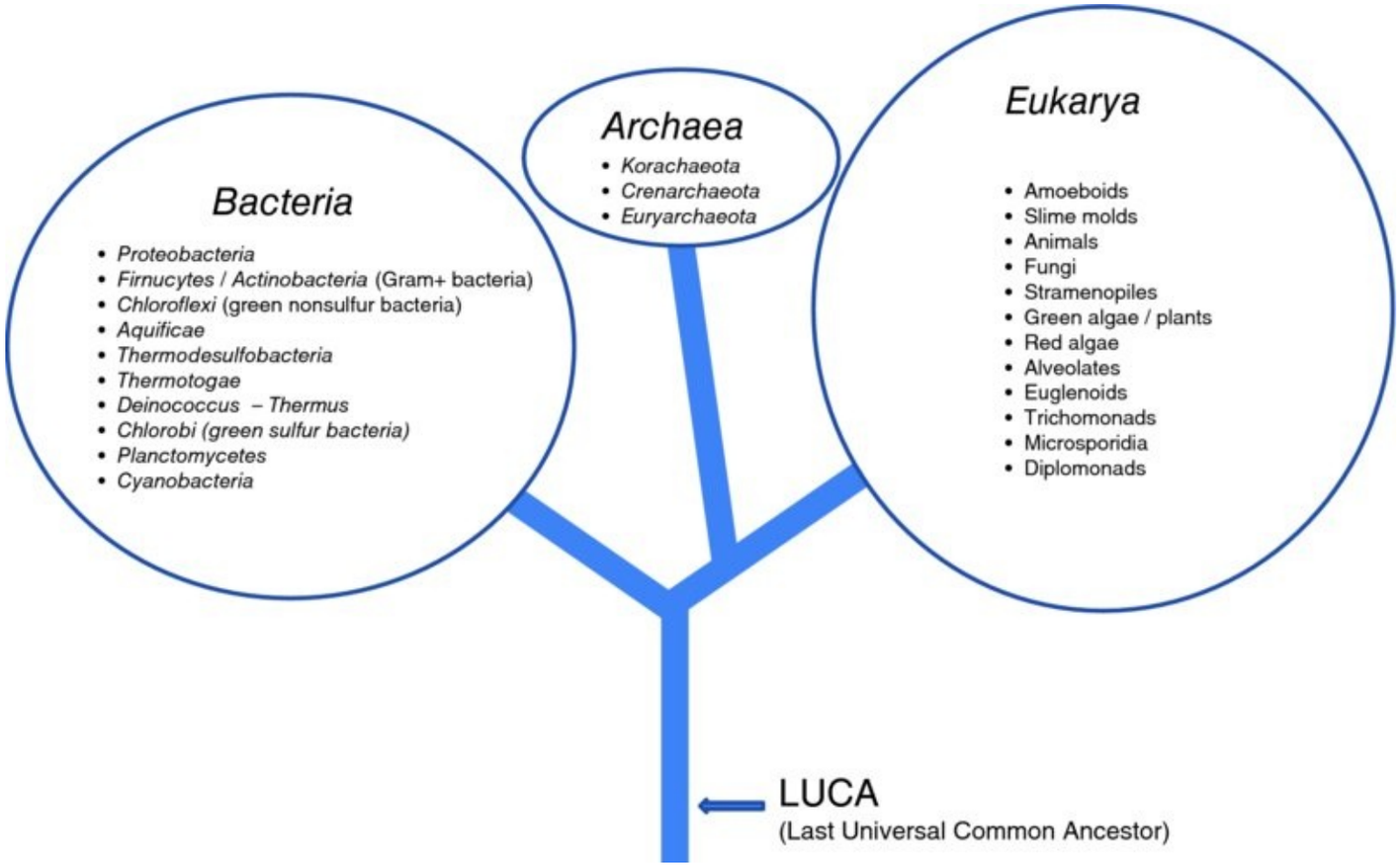


FIGURE 3.15 Phylogenetic tree based on 16S and 18S rRNA sequence comparisons. Branch lengths are not to scale. (Modified after Konhauser, 2007.)

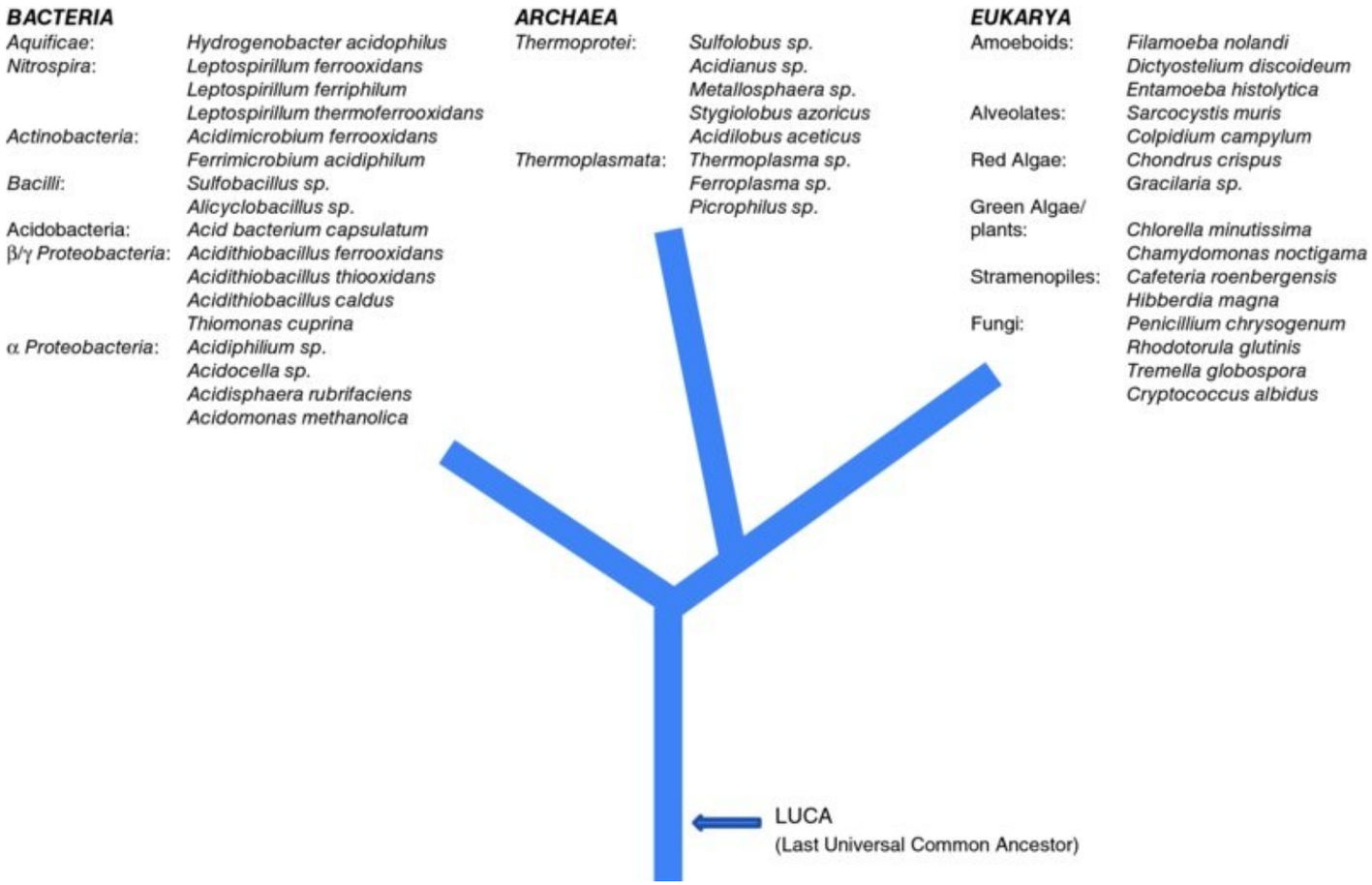


FIGURE 3.16 Phylogenetic tree based on 16S and 18S rRNA sequences for species identified in highly acidic waters. Branch lengths are not to scale. (Modified after Konhauser, 2007.)

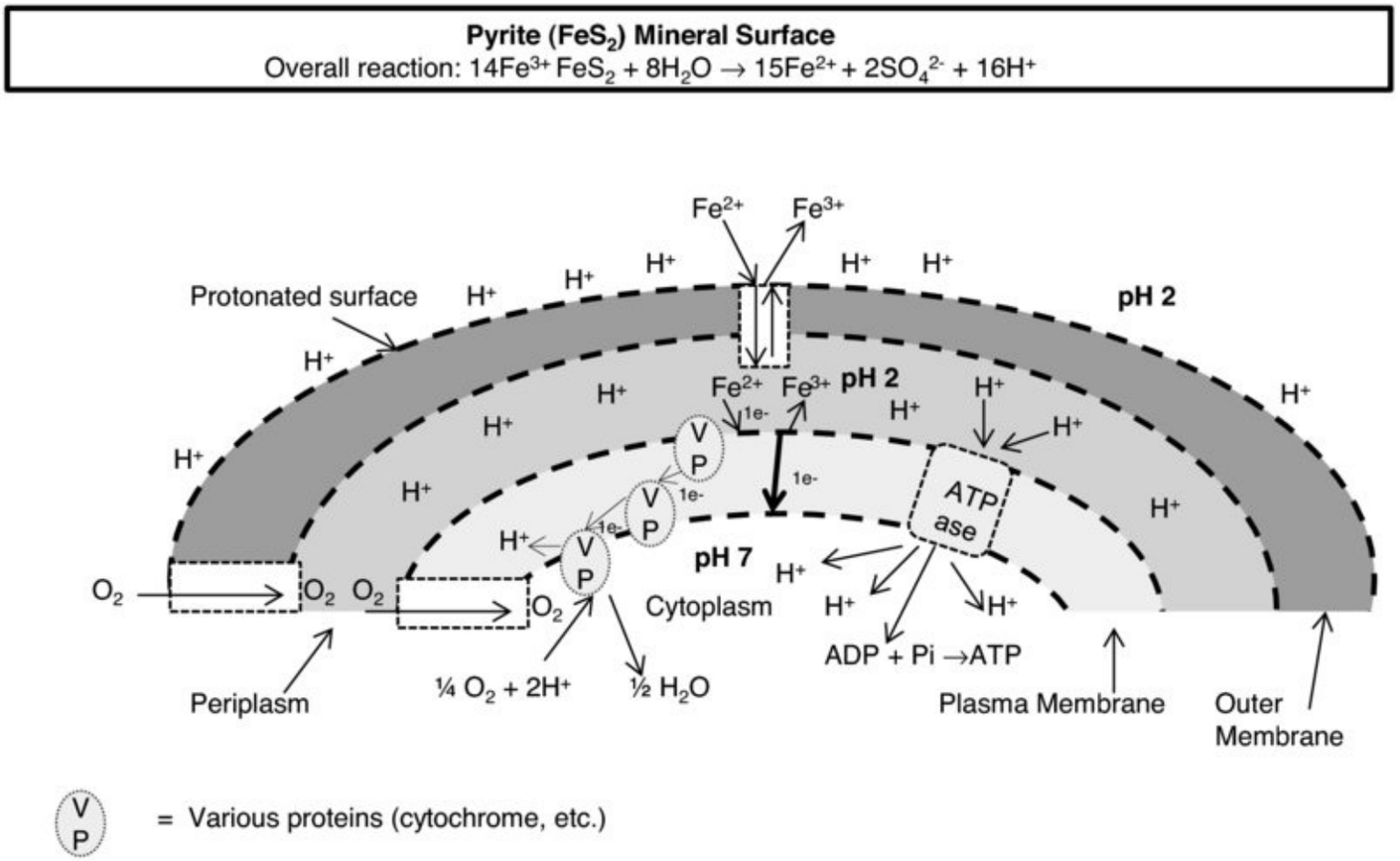


FIGURE 3.17 Cell membrane and electron transport chain and the generation of the proton motive force in acidophilic Fe(II)-oxidizing bacteria such as *A. ferrooxidans*. (Modified after Ingledew, 1977, and Konhauser, 2007.)

Phylogenetic Overview of Acid Drainage Bacteria

As noted by Madigan et al. (2008), many major lineages of bacteria, called *phyla*, are known from the study of laboratory cultures, and many others have been identified from retrieval and sequencing of rRNA genes from microbial communities in natural habitats, including acid drainage areas. The proteobacteria constitute the majority of known bacteria of scientific, medical, industrial, and agricultural significance, including bacteria that cause acid drainage. Sulfur- and iron-oxidizing bacteria include *Thilobacillus* and *Anchromatium* and are chemolithotrophic microbes. The genus *Thiobacillus* and close relatives are gram-negative rod-shaped bacteria, morphologically indistinguishable from most other gram-negative rods. Phylogenetically, the species of thiobacilli are scattered among the proteobacteria, with different species residing within the alpha, beta, and gamma classes. The sulfur compounds most commonly used as electron donors in chemolithotrophic metabolism of thiobacilli are H_2S, S^0, and $S_2O_3^{2-}$ (Madigan et al., 2008). According to Hedrich et al. (2011), the "iron bacteria" are a microbial community of morphologically and phylogenetically heterogeneous prokaryotes. While species of iron-oxidizing bacteria can be found in many different phyla, most are affiliated with the gamma proteobacteria (Emerson and Moyer, 1997).

Related to the production of acid drainage, several thiobacilli are acidophilic. *Achromatium* is a spherical sulfur-oxidizing chemolithotroph common in freshwater sediments that contain sulfide. Some sulfur chemolithotrophs are obligate chemolithotrophs. Carboxysomes are often present in cells of obligate chemolithotrophs. Other sulfur chemolithotrophs can grow either chemolithotrophically or chemoorganotrophically. Such a nutritional lifestyle is called *mixotrophy*. *Beggiatoa*, a filamentous

gliding sulfur-oxidizing bacterium, is found in nature primarily in habitats rich in H_2S. An interesting habitat is the rhizosphere of plants (rice, cattails, and other swamp plants) living in flooded, and hence anoxic, soils. *Beggiatoa* and other filamentous bacteria, such as *Sphaerotilus*, can cause major settling problems in sewage treatment facilities and in industrial waste lagoons. Other filamentous sulfur-oxidizing bacteria include *Thioploca* and *Thiothrix*. Cells of *Thioploca* can accumulate huge amounts of nitrate intracellularly, and this nitrate can then support extended periods of anaerobic respiration, with H_2S as an electron donor. *Thiothrix* is a filamentous sulfur-oxidizing organism that groups together to form cell arrangements called *rosettes* (Madigan et al., 2008).

Size of Microbes

Bacteria are typically 500 to 2000 nm (0.5 to 2 µm) in diameter. Some cyanobacteria are larger than 2000 nm, and some sulfide-oxidizing bacteria, such as *Thiovulum* and *Beggiatoa*, may be as large as 20,000+ nm. The smallest unicellular eukaryotes are measured at 2000 to 3000 nm, but most are 5 to one 100 times larger. Most microbes are unicellular, although some form communities that are filamentous, as is common in acid mine drainage settings. The ultrasmall microbes identified as archaeal Richmond mine acidophilic nanoorganisms are ellipsoiodal and measure only about 200 to 400 nm in diameter, which is about one-third the diameter of the ubiquitous rod-shaped *Escherichia coli* bacteria. Therefore, acidophiles can measure from 200 to 400 nm in diameter up to several times that size. The universal phyogenetic tree, based on the 16S and 18S rRNA sequence comparisons, shows bacteria, archaea, and eukarya, the three domains of life. Microbes were originally classified based on their preferred environments, food source, electron acceptors, and environmental conditions (Table 3.7). More recently, microbes have been studied and categorized based on 16S and 18S rRNA sequences.

TABLE 3.7 Summary of Microorganism Categories

Terminal Electron Acceptor(TEM) for CellularRespiration	Name	Description
Oxygen	Aerobe	Capable of using oxygen as a terminal electron acceptor; can tolerate a level of oxygen equivalent to or higher than the 21% oxygen present in an air atmosphere and has a strictly respiratory-type metabolism
All TEMs other than oxygen	Anaerobe	Grows in the absence of oxygen; some anaerobes have a fermentative-type metabolism; others may carry out anaerobic respiration in which a terminal electron acceptor other than oxygen is used
All TEMs, either with oxygen or other TEMs	Facultative anaerobe	Can grow aerobically or anaerobically—characteristic of a large number of genera of bacteria, including coliforms such as *Escherichia coli*
Low oxygen concentrations	Microaerophile	Capable of oxygen-dependent growth but only at low oxygen levels; cannot grow in the presence of a level of oxygen equivalent to that present in an air atmosphere (20.9% oxygen)

Synthesizers of Cell Mass	Cell Mass	Source of Material
Autotrophic	Carbon	Carbon dioxide (CO_2) is the sole source of carbon
Heterotrophic	Carbon	Carbon dioxide and one or more organic compounds
Mixotrophic	Carbon	Both organic compounds and by fixing carbon dioxide
Source of Electron Transfers	Examples	Source of Material
Lithotrophic	Iron-oxidizing bacteria *A. ferrooxidans* use Fe^{2+} as a source of electrons and energy: $Fe^{2+} \rightarrow Fe^{3+} + e^-$	Inorganic compounds rich in electrons; for iron-oxidizing bacteria, reduced iron (FeS_2) as pyrite is the source
Organotrophic	Microbes involved with composting	Humic material and wood
Source of Energy for Life andCellular Growth	Examples	Source of Material
Chemotrophic	Iron-oxidizing bacteria *A. ferrooxidans* use Fe^{2+} as a source of electrons and energy: $Fe^{2+} \rightarrow Fe^{3+} + e^-$	Chemoautotrophs use inorganic energy sources, such as hydrogen sulfide, elemental sulfur, ferrous iron, molecular hydrogen, and ammonia
Phototrophic	*Cyanobacteria:* Oxygenic photosynthetic organisms use chlorophyll for light-energy capture and oxidize water, generating molecular oxygen	Energy is obtained in the photic zone by light from the Sun in the ocean and surface water
pH of Environment	Name of Microorganism	Characteristics
	Acidophile	Grows at pH values less than 2
	Alkalophile	Grows at pH values greater than 10
	Neutrophile	Grows best at pH values near 7
Physiological CharacteristicDescription	Temperature	Description
	Psychrophile/facultative psychrophile	Optimal temperature for growth is 15°C or lower, maximal temperature is approximately 20°C, and minimal temperature is 0°C or lower
	Psychrotroph	Capable of growing at 5°C or below, with maximal temperature generally above 25 to 30°C; in this

		case the term is a misnomer because it does not indicate nutritional characteristics
	Mesophile	Generally defined by optimal temperature for growth, which is approximately 37°C; frequently grows in the range from 8 to 10°C and from 45 to 50°C
	Thermophile	Grows at 50°C or above
	Hyperthermophile	Grows at 90°C or above, although optimal temperature for growth is generally above 80°C; maximal growth of pure cultures occurs between 110 and 113°C, although the maximum (113°C) may well increase as further research is done
Salinity	Name of Microorganism	Characteristics
	Halophile	Requires salt for growth: extreme halophiles (all are archaea), 2.5 to 5 m salt
	Moderate halophiles	Usually low levels of NaCl as well as 15 to 20% NaCl
Hydrostatic pressure (100 atmper 1000 m of depth)	Name of Microorganism	Characteristics
	Obligate barophiles	No growth at 1 atm of pressure
	Barotolerant bacteria	Growth at 1 atm but also at higher pressures
	Barophilic	A number of deep-sea bacteria that grow optimally under pressure and grow optimally at or near their in situ pressure (0.987 atm = 1 bar = 0.1 MPa)
Compound Names	Name	Description
	Chemoorganoheterotroph	Derives energy from chemical compounds and uses organic compounds as a source of electrons; biomass is produced from organic compounds
	Chemolithoautotroph	Relies on chemical compounds for energy and uses inorganic compounds as a source of electrons; biomass is produced from carbon dioxide in five classes: hydrogen bacteria, iron bacteria, sulfur bacteria, ammonia oxidizers, and nitrite oxidizers; specific nutritional groups of bacteria that do not fit clearly in this category include obligate methane oxidizers and carbon monoxide oxidizers; there are also photoorganoheterotrophs and photolithoautotrophs among the anoxygenic photosynthetic bacteria
	Mixotroph	Capable of growing both chemoorganoheterotrophically and chemolithoautotrophically; examples include some

		of the hydrogen bacteria and some species of *Thiobacillus* (sulfur-oxidizing bacteria)
	Oligotroph	Can develop at first cultivation on media containing minimal organic carbon (1 to 15 µg of carbon per liter) and grow on such media in subsequent cultivation
	Copiotroph	Requires nutrients at levels 100 times those of oligotrophs

Groundwater Flow and Microbes

Aquatic organisms such as clams or fish rely primarily on advection or moving water as a physical transport mechanism to bring them into contact with food, nutrients, and terminal electron acceptors, such as oxygen, for cellular respiration. Groundwater advection is a main transport mechanism to move microbes in the subsurface through pore openings. However, on this scale, finer water movements are needed to bring the necessary resources to the microorganisms and microbial communities. Since microbes are at a scale of an individual cell, only molecular diffusion works to bring in nutrients, terminal electron acceptors for cellular respiration, and food sources or carbon dioxide for cellular growth. Molecular diffusion is the main transport mechanism at the microbial scale, modifying concentration gradients of terminal electron acceptors, nutrients, or other chemicals. Although microbes readily attach to mineral surfaces such as pyrite, a portion of them remain mobile in subsurface pore waters. The microbes move within the subsurface based on the hydrogeologic characteristics of the aquifer, such as hydraulic conductivity and gradient. The range of hydraulic conductivity of natural materials selected shows high variability based on lithological description (Figure 3.18). Even within one type of rock, fractured versus unfractured basalt makes a large difference in the range of hydraulic conductivity due to variations in permeability. In a fracture flow system, the flow rate under a given head is proportional to the cube of the fracture aperture; open fractures can support significant flow. Permeability, groundwater gradient, lithology (including the amount of clay and organic material), heterogeneity of the aquifer, location of geologic faults, tidal influences near shorelines, and other factors affect groundwater flow and microbial distribution and transport in the saturated zone.

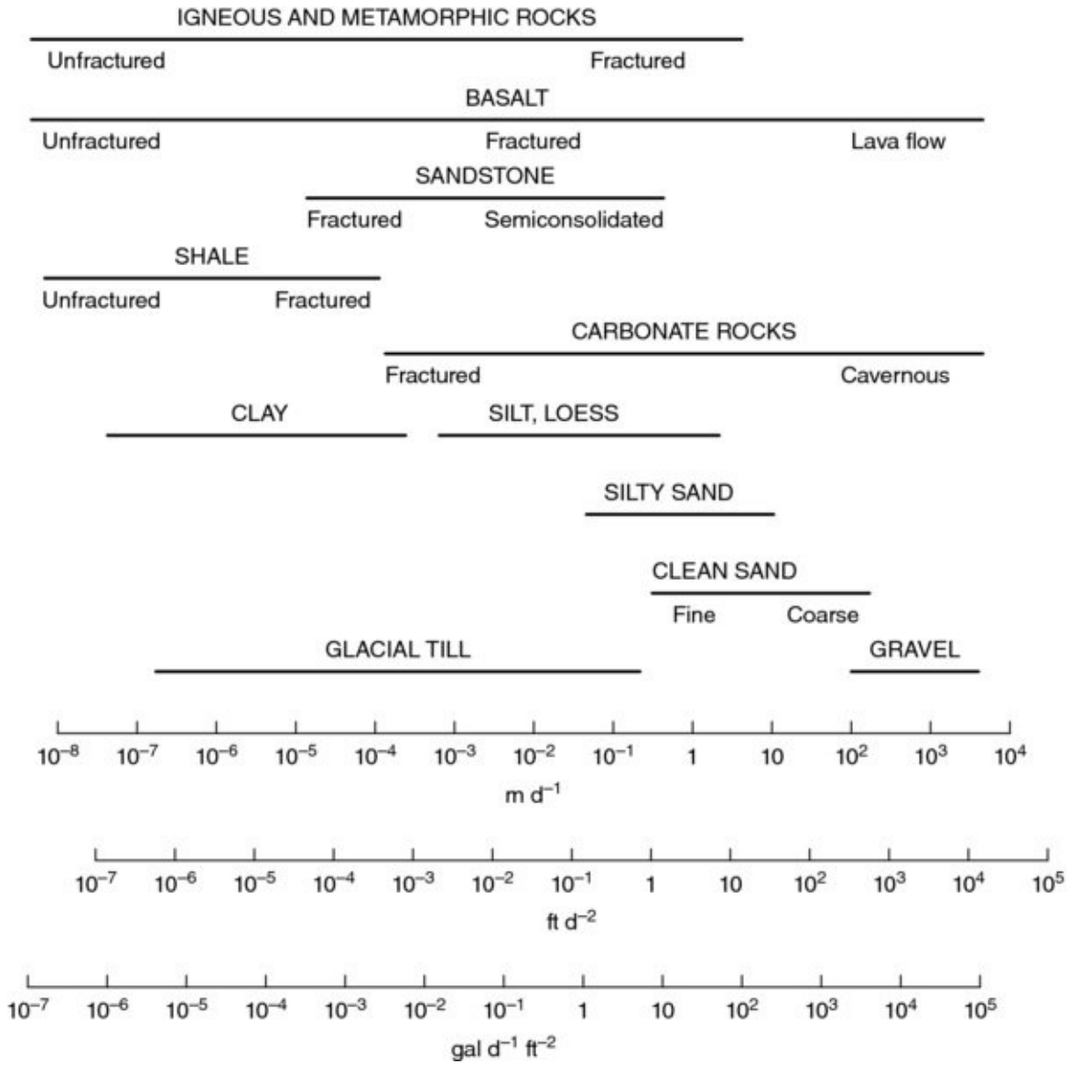


FIGURE 3.18 Hydraulic conductivity affects groundwater flow and the ability to transport microorganisms through the connected pore openings. (After Heath, 1983.)

Groundwater flow is related to advection and dispersion. *Advection* describes mass transport due simply to the bulk *Flow* of water. The microbes can migrate with the groundwater flow. *Dispersion*refers to the spreading and mixing caused by molecular *Diffusion*. Diffusion gradients allow groundwater, with microbes, to move on a small, molecular scale. Diffusion allows groundwater to move from a higher concentration area to an area of lower concentration. The concentrations can relate to metals concentrations, acidity, colloidal-based turbidity, or other parameter where concentration is a driving force. Diffusion allows groundwater to migrate from areas with higher metal concentrations, higher acidity, or higher turbidity areas toward areas of lower metal concentrations, lower acidity, or lower turbidity areas, respectively. Groundwater movement within the pore spaces is an important factor in microbial dispersion in the saturated zone. Microbial movement in the saturated zone may be either laminar or turbulent. In laminar flow, microbes move in an orderly manner along streamlines (Figure 3.19). In turbulent flow, microbes move in a disordered, highly irregular manner, which results in a complex mixing of the microbes. Under natural hydraulic gradients, turbulent flow occurs only in large pore throat openings such as those in gravel, lava flows, and limestone caverns. Flows are laminar in most granular deposits, such as sandstones and fractured rocks. In laminar flow in a granular medium such as sand, the different streamlines converge in the narrow necks between microbes and diverge in the larger interstices. There is some intermingling of streamlines, which results in transverse dispersion at right angles to the direction of groundwater flow. Differences in velocity result from friction between the

water and the microbes as well as rock particles that have been transported. Assuming high connectivity between the connected pore openings, also called high permeability, the fastest flow rate of the larger microbes occurs in the center of larger pore throat openings. The resulting dispersion is longitudinal or in the direction of flow.

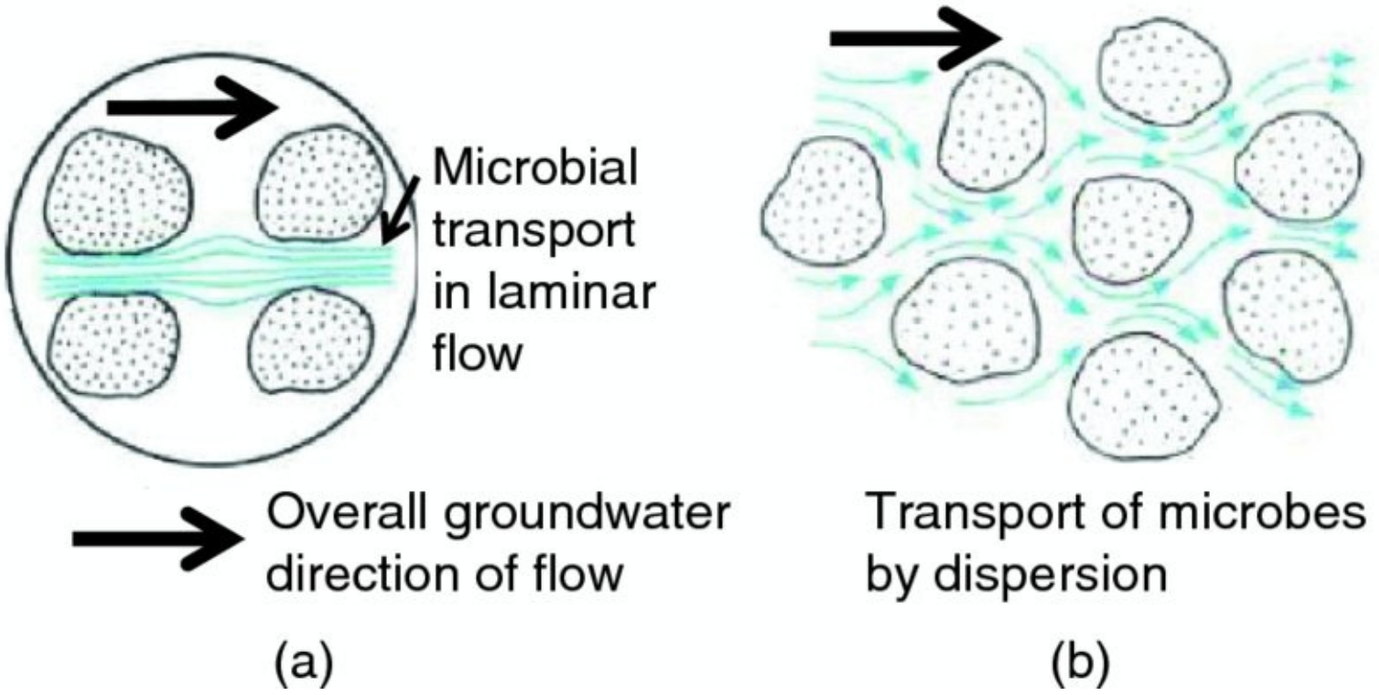


FIGURE 3.19 (a) Laminar flow, with groundwater moving from left to right; (b) dispersion in a granular deposit transports microorganisms through the connected pore openings. (Modified after Heath, 1983.)

The higher groundwater flow rates (i.e., the more rapidly the sediment is flushed with the groundwater) lead to higher levels of microbial elution (Trevors et al., 1990). Under high flow rates, microbial transport rates have been reported to be over 200 m/day (Keswick et al., 1982). Even under stagnant conditions or where groundwater exhibits no flow, some motile microbes can move through packed sand cores at rates greater than 0.1 m/day (Reynolds et al., 1989). Field measurements of microbial movement compared to chemical tracers even indicate that some microorganisms will travel through the larger, preferred higher-flow, more laminar pathways rather than through the more tortuous and slower pathways. Consequently, microorganisms may preferentially be transported in a larger, more direct pathway through the aquifer than through the smaller, more tortuous pathways taken by chemical tracers in the groundwater (Harvey et al., 1989). Microbes tend to accumulate preferentially at the gas–water interface, at the base of the vadose zone, and this can impede movement (Wan et al., 1994).

Microbial Growth Conditions

Optimal conditions for microbial growth and colony expansion include available carbon sources, terminal electron acceptors, nutrients, and proper temperature, pressure, salinity, and pH. Carbon in the form of carbon dioxide (for autotrophs) or organic compounds (for heterotrophs) is one requirement for robust microbial growth. Energy for the microbe is derived from a redox reaction in which electrons are transferred from the electron donor, frequently hydrogen (H^+), to a terminal electron acceptor such as oxygen, which wants to fill the outermost electron shell with two electrons donated from hydrogen. When oxygen is the electron acceptor, the process is called *aerobic*. Oxygen provides the highest level of energy

compared to all other terminal electron acceptors, and aerobic microbes have the most cellular energy from the process. A schematic based on Konhauser (2007) shows the approximate electrode potentials of the major environmental terminal electron acceptors (TEAs) (Figure 3.20).

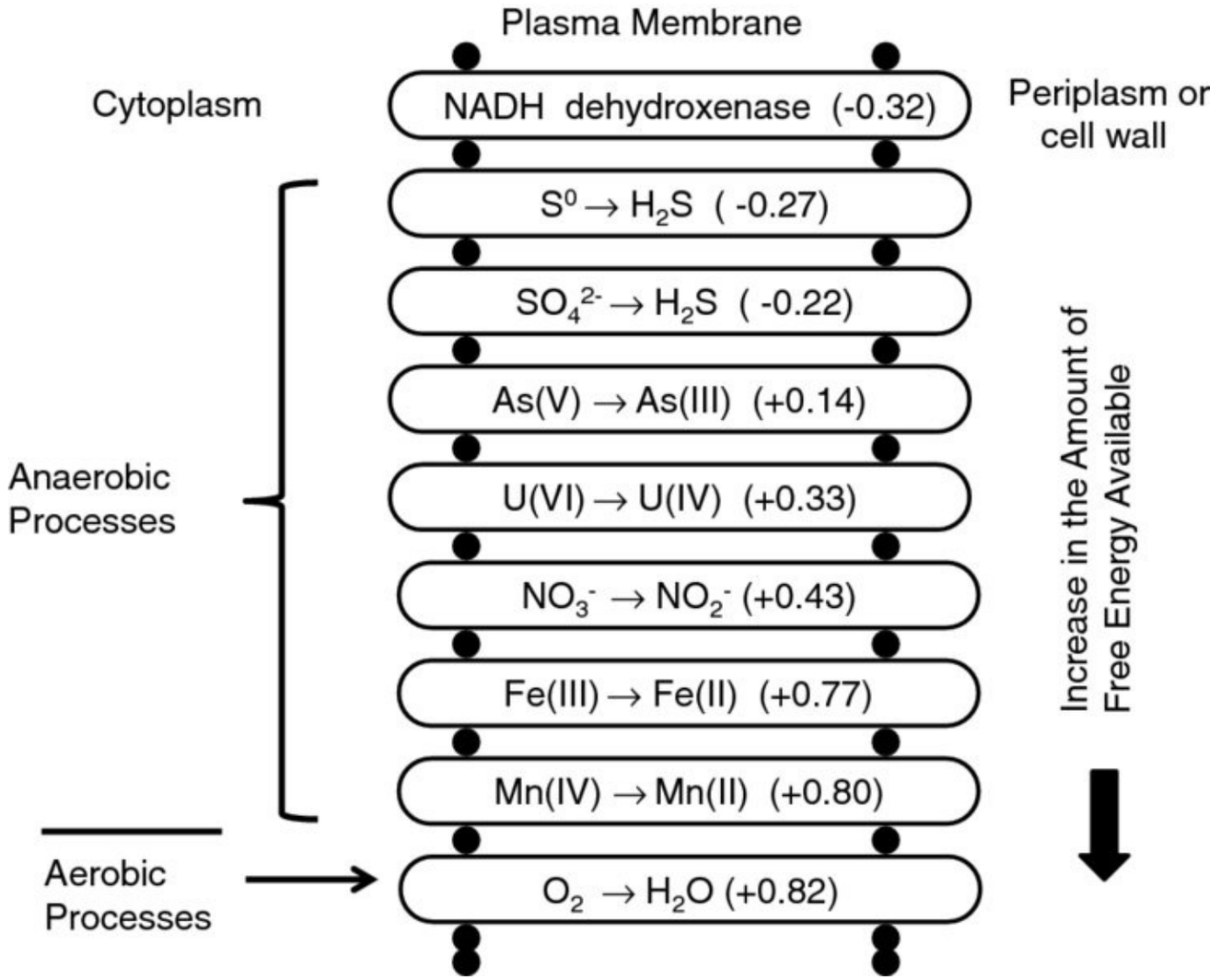


FIGURE 3.20 Approximate free energy for major terminal electron acceptors. Not to scale. (Modified after Konhauser, 2007.)

In this case, the primary electron donor in chemoheterotrophic metabolism is nicotinamide adenine dinucleotide phosphate (NADH). The amount of free energy in a particular metabolic redox reaction is based on the difference between the electode potential of the primary electron donor, which is NADH (−0.32), and the terminal electron acceptor. Using oxygen as the terminal electron acceptor with the highest electrode potential (+0.82), the energy for the NADH–O_2 metabolic coupling yields an increase to +1.14, compared to the lower-energy NADH–SO_4^{2-} metabolic coupling, which yields an energy increase of +0.10. Facultative microbes can use oxygen or other terminal electron acceptors. In the presence of oxygen, strictly anaerobic microbes do not survive. For microbial processes (see Figure 3.13) not using oxygen as the primary terminal electron acceptor, manganese [Mn(IV)], ferric iron [Fe(III)], nitrate (NO^{3-}), uranium [U(VI)], arsenic [As(V)], sulfate (SO_4^2), and sulfur (S^0) are used. Other TEAs not shown in Figure 3.13 include carbon dioxide (CO_2) or other less common electron acceptors, such as cobalt [Co(III)] and fumarate ($C_4H_4O_4$), and halogenated organic compounds such as tetrachloroethylene (PCE; C_2Cl_4) and trichloroethylene (TCE; C_2HCl_3) are used. Detailed studies have been performed (Holliger

et al., 1998a,b) showing that the energy metabolism of anaerobic bacteria is lower than that of those that utilize aerobic processes. When oxygen is introduced into an anoxic environment where anaerobes or facultative microbes predominate, microbes that can metabolize oxygen will dominate the nanoenvironment. Until the oxygen is consumed, the oxygen will become the predominant electron acceptor. Once the oxygen is consumed, the microbes that can generate the most energy from the existing remaining terminal electron acceptors will dominate the nanoenvironment. As terminal electron acceptors offering the highest level of energy are consumed, the oxidation and reduction processes change over time, generally getting less energetic, until there is a new influx of terminal electron acceptors with a higher energy potential.

Macronutirent and micronutrient availability such as nitrogen and phosphorus are also essential for microbial growth and in excess can support excess growth. Cells are made of several chemical elements. The six major elements needed by most microbes are carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulfur. Other important elements are potassium, calcium, iron, magnesium, and sodium. Also important for the microbe cell structure are the trace elements cobalt, zinc, copper, and manganese. For temperature, most bacteria demonstrate optimal growth below approximately 70°C.

The energy budget for iron- and sulfide-oxidizing bacteria exceeds most other bacteria found in groundwater. In fact, iron-oxidizing bacteria, responsible for the slimy coatings of ferric iron that sometimes encrust wells, obtain energy for growth from reaction (3.5). The energy released is about 160 kcal. Iron oxidation obtains relatively little energy per mole of substrate oxidized (40 kcal/mol Fe^{2+}) compared to sulfide oxidation (150 kcal/mol H_2S) or even hydrogen oxidation (56 kcal/mol H_2). A simple analogy illustrates the core of this energy difference; taking sulfide to sulfate involves the transfer of eight electrons. In contrast, taking ferrous iron to ferric iron involves only one electron. Fewer electrons transferred per reaction means that, overall, to maintain a proper energy flux more atoms must participate in the process. Iron-oxidizing bacteria are therefore required to turn large amounts of Fe^{2+} into Fe^{3+} to obtain sufficient energy to sustain growth. In wells and in acid drainage deposits, this means that the iron-oxidizing bacteria accelerate the geochemical process to produce large volumes of highly insoluble ferric oxyhydroxides (Chapelle, 1993). It is these large volumes of ferric oxyhydroxides produced by iron-oxidizing bacteria that make it difficult to stop acid drainage once it starts, regardless of source. The biogeochemical process makes drinking water well maintenance a significant challenge in areas having large volumes of soluble iron in the groundwater with abundant iron-oxidizing bacteria. Sulfide oxidizers, although not as ubiquitous as iron bacteria in groundwater, have been observed in coal spoil piles producing acid mine drainage.

A summary of sulfur-metabolizing microbes includes all three phylogenetic domains of life (Table 3.8). Microbial naming terms are often combined, as shown in the table. Chemolithoautotrophs obtain their energy from the oxidation of inorganic compounds and carbon from the fixation of carbon dioxide. Examples of chemolithoautotrophs include nitrifying bacteria, sulfur-oxidizing bacteria, iron-oxidizing bacteria, and *Knallgas* bacteria, which oxidize hydrogen. Sulfur- and iron-oxidizing bacteria are associated with acid drainage and have been identified in highly acidic waters. Photolithoautotrophs obtain their energy from light and carbon from the fixation of carbon dioxide, using reducing equivalents from inorganic compounds. Examples include cyanobacteria using water (H_2O) as a reducing equivalent donor; Chlorobiaceae; Chromatiaceae using hydrogen sulfide (H_2S) as a reducing equivalent donor; and Chloroflexus using hydrogen (H_2) as a reducing equivalent donor. Photolithoautotrophs have not been identified in highly acidic waters.

TABLE 3.8 Summary of Sulfur-Metabolizing Microorganisms Among Major Phylogenetic Lineages[a]

Archaea
Crenarchaeota
Thermoproteales; SR
Desulfurococcales; SR
Sulfolobales; C
Euryarchaeota
Archaeoglobales; SUR
Thermococcales; SR
Thermoplasmatales; SR
Some methanogens; OSU (e.g., *Methanosarcina*; OSU)
Bacteria
Aquificae
Aquifex; C, *Persephonella*; C
Sulfurihydrogenibium; C
Desulfurobacterium; SR, *Thermovibrio*; SR
Balnearum; SR
Chloroflexaceae
Chloroflexus; PSO
Chlorobiaceae; PSO
Nitrospiraceae
Thermodesulfovibrio; SUR
Thermodesulfobacteriaceae
Thermodesulfatator; SUR
Thermodesulfobacterium; SUR
Firmicutes
Desulfotomaculum; SUR
Desulfosporosinus; SUR
Ammonifex; SR
α-Proteobacteria
Roseobacter-clade, SAR-11; OSU
Paracoccus; C
Various genera (e.g., *Rhodobacter*; PSO)
Rhodospirillum; PSO, *Rhodomicrobium*; PSO
β-Proteobacteria
Acidithiobacillus (*Thiobacillus*); C, *Thiomonas*; C
Alcaligenes; OSU

Rubrivivax; PSO, *Rhodocyclus*; PSO, *Rhodoferax*; PSO
γ-Proteobacteria
Various genera; C (e.g., *Thiomicrospira*; C, *Beggiatoa*; C, *Thioploca*; C, *Thiomargarita*; C)
Symbionts of invertebrates; C (e.g., *Riftia*; C, *Calyptogena*; C)
Methylophaga; OSU, *Pseudomonas:* OSU, unidentified γ-proteobacteria; OSU Chromatiaceae; PSO, Ectothiorhodospiraceae; PSO
δ-Proteobacteria
Various genera; SUR (e.g., *Desulfovibrio*; SUR, *Desulfotalea*; SUR, *Desulfonema*; SUR, *Desulfosarcina*; SUR, *Desulfobacter*; SUR, *Desulfuromonas*; SR, *Desulfurella*; SR, *Desulfuromusa*; SR, *Geobacter*; SR)
Some sulfate reducers; OSU (e.g., *Desulfovibrio*; OSU)
ε-Proteobacteria
Arcobacte; C, *Thiovulum*; C, *Sulfurimonas*; C, *Sulfurovum*; C
Various genera; SR (e.g., *Sulfurospirillu*; SR), *Nautilia*; SR, *Caminibacter*; SR

Source: Based on the work of Giovannoni and Stingl (2005) and Sievert et al. (2007).

[a]PSO, prototrophic sulfur oxidizers; C, chemolithotrophic; SO, sulfur oxidizers; SR, sulfur reducers; SUR, sulfate reducers; OSU, organic sulfur utilizers.

Chemolithoautotrophs require carbon dioxide (CO_2) for growth. *Acidithiobacillus*, previously called *Thiobacilus*, is an example; another is the denitrifying *Nitrobacter* spp. Chemolithoheterotrophs cannot fix carbon dioxide; an example is *Beggiatoa*. Both autotrophic and heterotrophic chemolithotrophs obtain their energy from the oxidation of inorganic compounds such as pyrite. Examples include some *Wolinella* using H_2 as a reducing equivalent donor, some *Knallgas* bacteria, and some sulfate-reducing bacteria. Some chemolithotrophics, such as *A. ferrooxidans*, are airborne bacteria and some are associated with acid drainage. This genus is thermophilic, preferring temperatures of 45 to 50°C. *Acidithiobacillus* is a genus made up of numerous species that have been identified in highly acidic waters. Many of the *Acidithiobacillus* species prefer a pH of 1.5 to 2.5. A few species, however, grow only in a neutral pH and are likely to be associated with the initiation of pyrite oxidation at a circumneutral pH.

Chemoorganoheterotrophs obtain their energy, carbon, and reducing equivalents for biosynthetic reactions from organic compounds. Examples include bacteria such as *Escherichia coli*, *Bacillus* spp., and *Actinobacteria*. *A. ferrooxidans* and *Ferrimicrobium acidiphilum* are *actinobacteria* that have been identified in highly acidic waters. Photoorganoheterotrophs obtain their energy from the light of the sun, carbon, and reducing equivalents for biosynthetic reactions from organic compounds such as compost. Some species are strictly heterotrophic, and many others can also fix carbon dioxide and are mixotrophic. Examples include *Rhodobacter*, *Rhodopseudomonas*, *Rhodospirillum*, *Rhodomicrobium*, *Rhodocyclus*, *Heliobacterium*, and *Chloroflexus*. These species have not been identified in highly acidic waters.

Acidophiles

Acidophilic iron-oxidizing proteobacteria were discovered in the late 1940s by Colmer et al. (1950), who identified *Acidithiobacillus ferrooxidans*. Other bacterial classifications were made by Woese (1987) and by Kelly and Wood (2000). Although most acidophiles can obtain their energy from the oxidation of reduced iron (Fe^{2+}) alone, when combined with the reduction of molecular oxygen, most

acidophilic species are, in fact, facultative anaerobes that can couple the oxidation of reduced sulfur compounds such as pyrite and in some cases hydrogen to the reduction of ferric iron (Fe^{3+}) in anoxic environments (Hedrich et al., 2011).

The most widely studied of all iron-oxidizing bacteria is an autotrophic acidophile, *Acidithiobacillus*, which is a genus of the *proteobacteria*. Like all proteobacteria, *Acidithiobacillus* is gram negative. The members of this genus were classified in the literature as *Thiobacillus* before they were reclassified by Kelly and Wood (2000). *Acidithiobacillus ferrooxidans* (also called *Thiobacillus ferrooxidans*) lives on the surfaces of sulfide deposits and metabolizes iron and sulfur to produce sulfuric acid. Another acidophilic bacterium associated with acid drainage (but also with other environments), *A. thiooxidans* (also called *Thiobacillus thiooxidans* and *T. concretivorus*), consumes sulfur and generates sulfuric acid (Hedrich et al., 2011).

While the iron-oxidizing bacteria are found in many different phyla, most are affiliated with the proteobacteria, which includes (1) acidophilic aerobic iron oxidizers, (2) neutrophilic aerobic iron oxidizers, (3) neutrophilic anaerobic and nitrate-dependent iron oxidizers, and (4) anaerobic photosynthetic iron oxidizers. The acidophilic aerobic iron oxidizers are the bacteria associated with acid drainage. Depending on ecosystem conditions and geochemistry, some species, mostly acidophiles, can reduce the oxidized form of iron (ferric or Fe^{3+}) as well as oxidize the reduced form of iron (ferrous or Fe^{2+}) (Hedrich et al., 2011).

Acidophiles are microorganisms that can thrive in highly acidic ecosystems with a pH of less than 3 and have been known to exist at pH values below zero, as in the Richmond mine in northern California at Iron Mountain. Acidophilic microorganisms can be found in all three domains of life: bacteria, archaea, and eucarya (Figure 3.20). An example of a common acidophile is *Acidithiobacillus thiooxidans*, which is a bacterium that cannot grow at pH values above 4 to 6, and growth for the microbe is still possible to a pH of 0.5, according to Kelly and Wood (2000). Acidophilic microbes keep their cytoplasm at a pH value near 7 by using powerful proton pumps in their cytoplasmic membrane. To accomplish the nearby neutral conditions in the cytoplasm, the microbes have to maintain a proton concentration gradient of four, five, or even more orders of magnitude. The intracellular enzymatic processes do not require special adaptations to low pH values. The ability of the microbial cells to withstand low pH values is controlled by the pH-resistant cell envelope that separates the highly acidic environment that acidophiles often require, and the intracellular compartment, which stays at a nearly neutral pH value (Rainey and Oren, 2006).

Review of Microbial Processes

According to Konhauser (2007), *A. ferrooxidans* uses cation bridging (starting point) to fix itself onto high-energy sites of the pyrite (FeS_2) surface (Figure 3.21). The process begins with salt bridging between the bacterium and the phosphate-enriched mineral surface. This tight junction is critical due to the small volume (about 0.009 μm^3) created between the bacterium and the pyrite surface, which helps the microbe establish an acidic nanoenvironment in this small interface (Mielke et al., 2003). A salt bridge is created between the bacterium and the phosphate-enriched pyrite mineral surface. An acidic nanoenvironment between the bacterium and the mineral surface is critical in dissolving the pyrite. The bacterium then excretes extracellular polymers (EPs) to provide additional adhesion (step 1) to the pyrite mineral surface (Figure 3.21). Dissolution of the pyrite under the bacterium in step 3 causes the release of sulfoxy anions (S_2OH^-) within the iron-rich EPs (Figure 3.22), while Fe^{2+} oxidizes to Fe^{3+}. Oxidation of the sulfoxy anions and hydrolysis of Fe^{3+} generate acidity that remains confined to the extracellular

polymers. The buildup of the iron–hydroxide minerals around the bacterium on the neutral side of the acid–neutral interface as corrosion is begun; helps maintain the acidic nanoenvironment at the cell–mineral contact by limiting the molecular diffusion of the acid or iron away from the microbe. Continued growth of the bacterium outward across the pyrite mineral surface and inward as the pyrite is being consumed as the source of energy for the microbe will eventually result in cell division (Mielke et al., 2003).

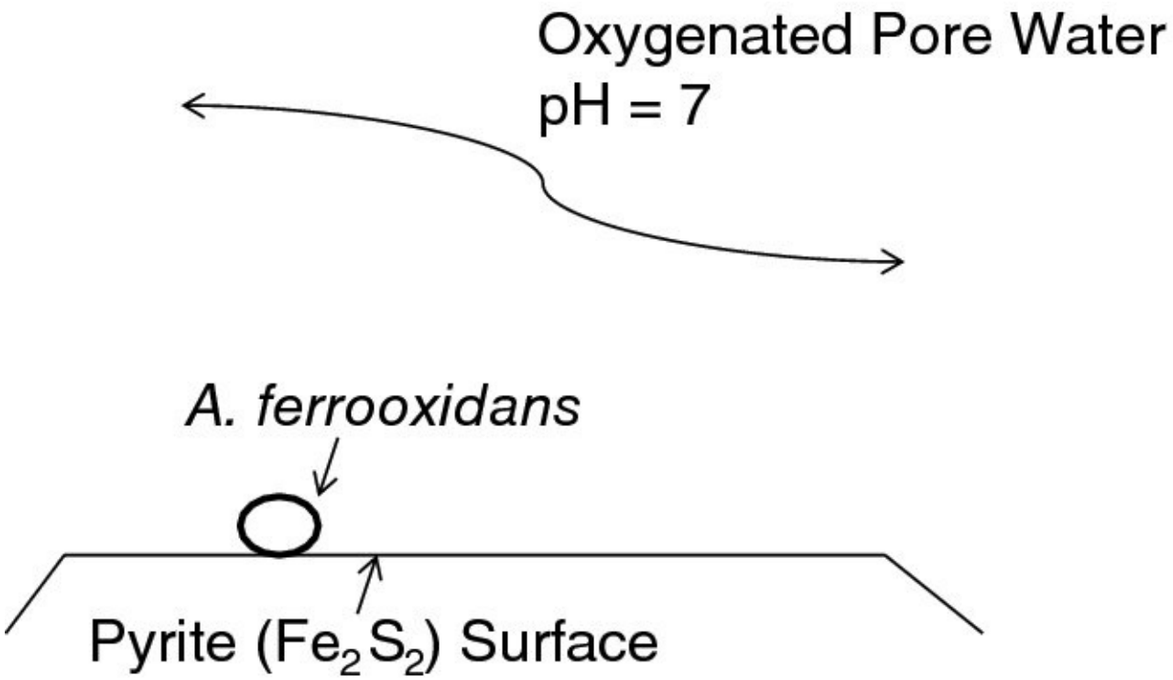


FIGURE 3.21 Starting point conceptual diagram of colonization of pyrite under circumneutral pH. Not to scale. (Modified after Southam and Beveridge, 1992; Mielke et al., 2003; and Konhauser, 2007.)

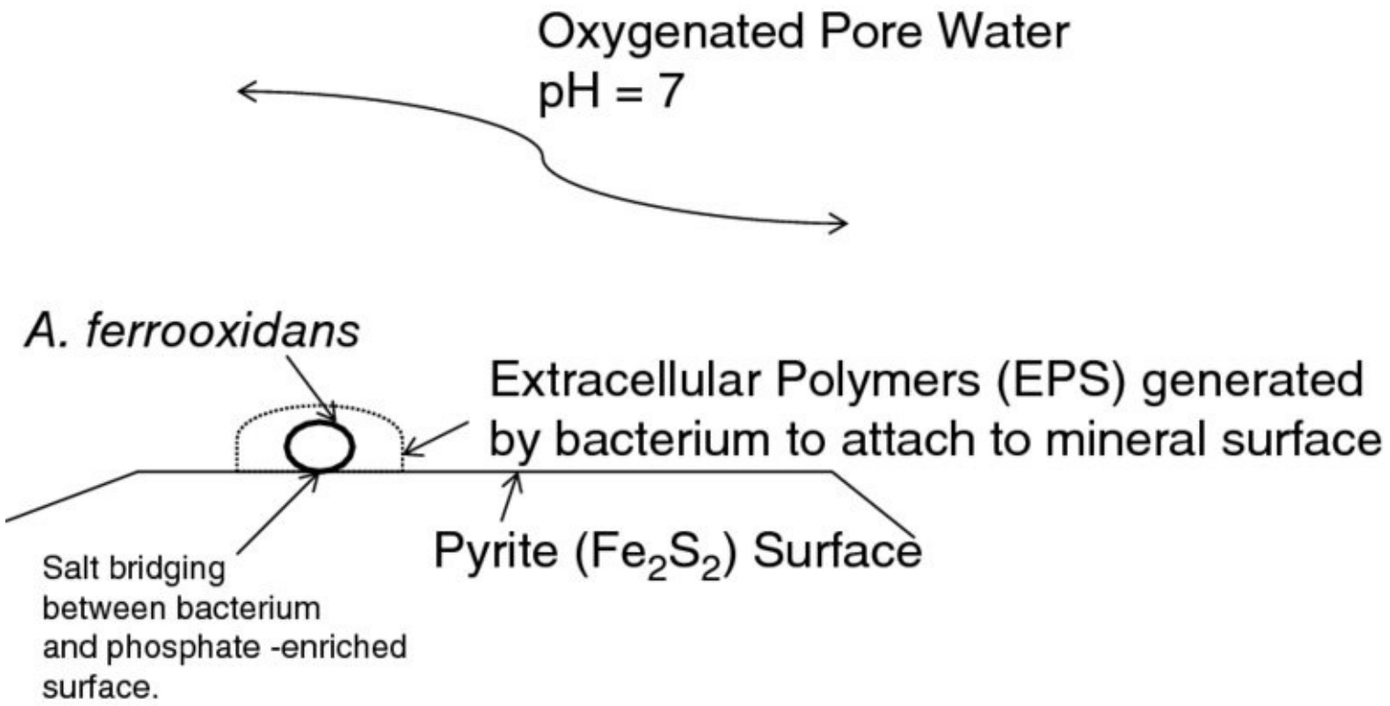
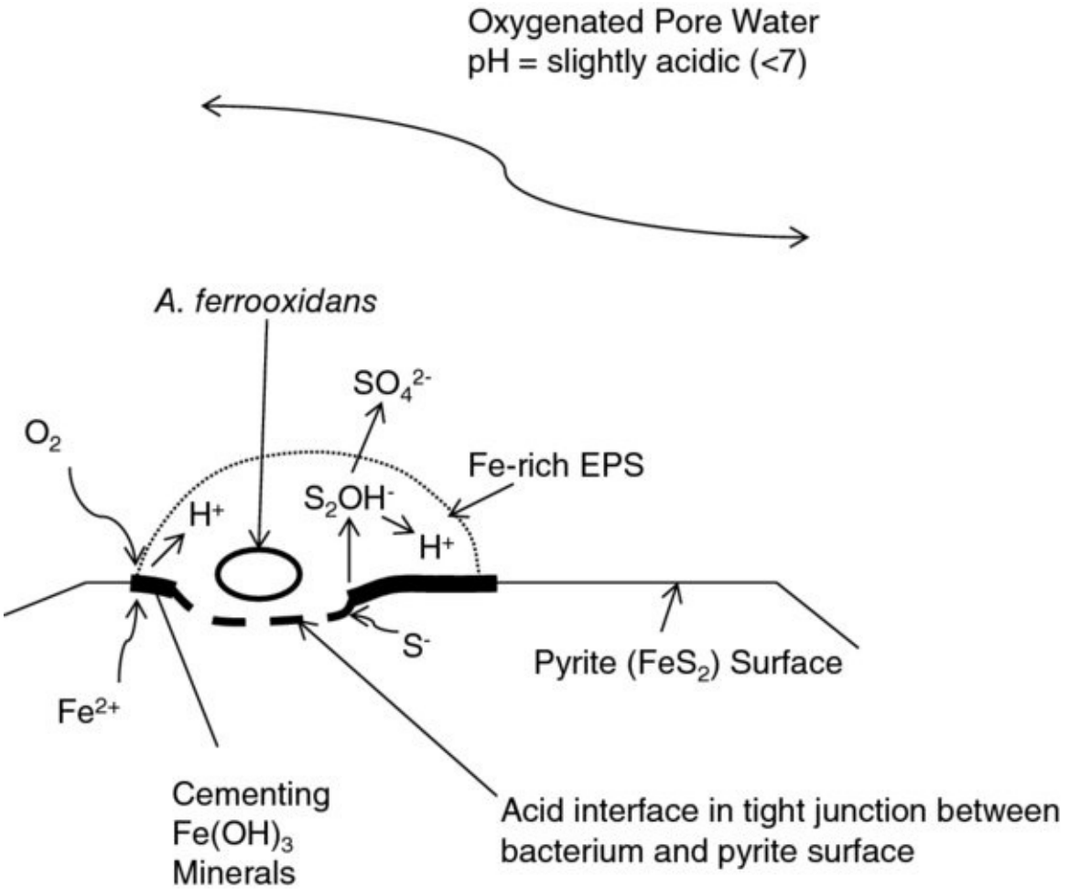


FIGURE 3.22 Conceptual diagram of the colonization of pyrite under circumneutral pH. Not to scale. (Modified after Southam and Beveridge, 1992; Mielke et al., 2003; and Konhauser, 2007.)

As the hydrogen ions are released (step 3) an acid expansion front is established and bacteria cells continue to multiply (Figure 3.23). The ferric hydroxide [$Fe(OH)_3$] redissolves to re-create Fe^{3+}, which reacts with the pyrite. At the same time, elemental sulfur (S^0) becomes a stable solid layer to which other acidophilic bacteria species, such as *A. thiooxidans*, can attach (see Figure 3.24). During this process, as the acid is generated, corrosion pitting of the pyrite mineral grains occurs. These small pits in pyrite surfaces provide locations for more acidophilic cells to attach to as the microcolony grows. The acidity is caused by the biological oxidation of the sulfoxy anions to the soluble sulfate ions, and a hydrogen ion is given off, creating an acid expansion front (see Figure 3.21). The acid front is also enhanced by the ferric hydroxide precipitation, which releases hydrogen ions as well. The precipitation of the ferric hydroxide that coats the pyrite surface becomes embedded within the expanding EPs. Later, a partial diffusion barrier is created by the ferric hydroxide and EPs, which maintains the hydrogen ions (H^+) in a nanoenvironment at the pyrite mineral surface. Konhauser (2007) estimates the partial diffusion barriers and nanoenvironment at the pyrite mineral surface to be a few cubic nanometers in volume. As the process continues to evolve and conditions become more favorable for acidophilic microbes, microcolonies are created as the bacteria continue to multiply. The microcolonies are enshrouded in the iron-rich biofilm. As the proximal pH drops, elemental sulfur (S^0) precipitates instead of the intermediate sulfur anions diffusing away. The precipitation of the elemental sulfur (see Figure 3.24) creates new opportunities for sulfur-oxidizing bacteria with an easily accessible oxidizable substrate, such as *A. thiooxidans*. Simultaneously, ferric hydroxide begins partial solubilization. The Fe^{3+} formed then reacts with the pyrite mineral surface to initiate the propagation cycle. This cycle extends the acidity to areas away from the immediate surroundings, which eventually affects the more neutral bulk pore water and is likely to be in the pH range 6 to 8.



Critical Equation for pH drop:

$$S_2OH^- + 3O_2 + H_2O \rightarrow 2SO_4^{2-} + 3H^+$$

FIGURE 3.23 Conceptual diagram of the colonization of pyrite. Not to scale. (Modified after Southam and Beveridge, 1992; Mielke et al., 2003; and Konhauser, 2007.)

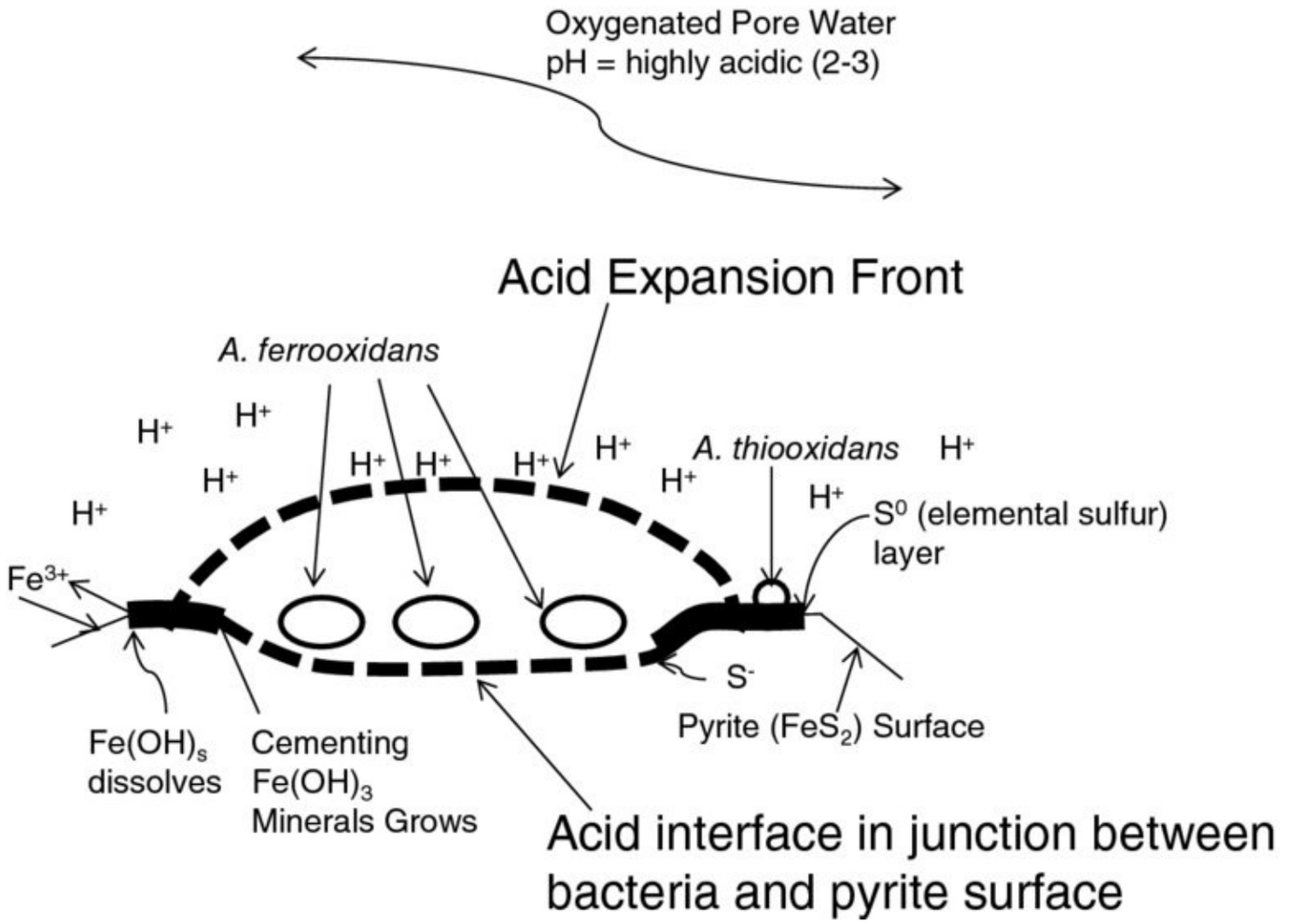


FIGURE 3.24 Conceptual diagram of the colonization of pyrite. Not to scale. (Modified after Southam and Beveridge, 1992; Mielke et al., 2003; and Konhauser, 2007.)

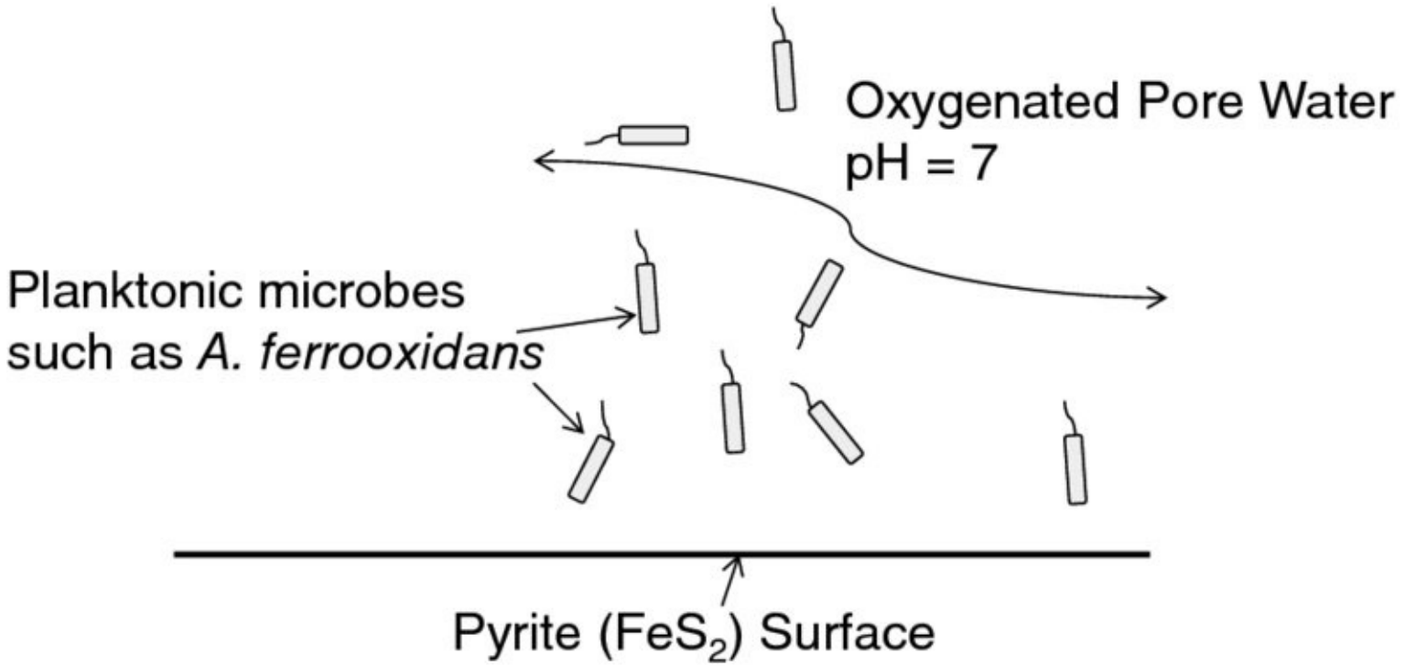


FIGURE 3.25 Step 1: Planktonic bacteria cells in pore fluids or surface waters. Including movement toward the pyrite surface. Not to scale.

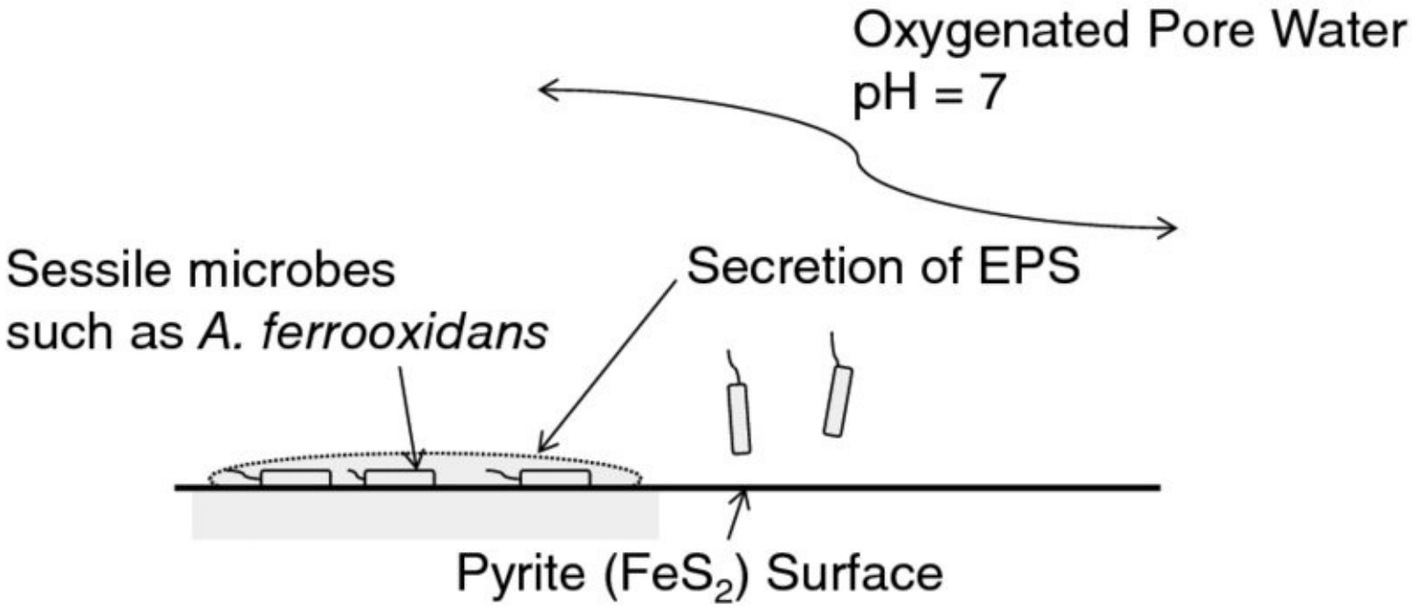


FIGURE 3.26 Step 2: Surface colonization starts as *A. ferrooxidans* attaches to pyrite, becoming sessile. Bacteria secrete extracellular polymers to attach to the mineral surface. Not to scale.

The transport mechanisms of *A. ferrroxidans* in a circumneutral pore water shows planktonic bacteria cells in pore fluids (Figure 3.25). Individual bacteria excrete EPs to attach to the iron sulfide mineral surface (Figure 3.26). Microcolonies of *A. ferrooxidans* develop the biofilm, and the pH in the oxygenated pore water outside the EPs becomes acidic. As noted by Mielke et al. (2003), there is an acidic nanoenvironment in the interface between the microbe and the pyrite mineral surface. Other acidophilic microbes, such as *A. thiooxidans*, later attach to the pyrite mineral surface as the pH value is maintained at 2 to 3.

As the *A. ferrooxidans* microcolony expands over time, the biofilm matures (Figure 3.27). Eventually, a portion of the main microcolony detaches with bacteria and EPs to migrate to another location and the process repeats itself. Seeding dispersal also continues with a single bacterium migrating as planktonic cells and the process repeats itself (Figures 3.28and 3.29). Migration is necessary if nutrients, dissolved oxygen, carbon sources, or other key resources are not being supplied and have been consumed.

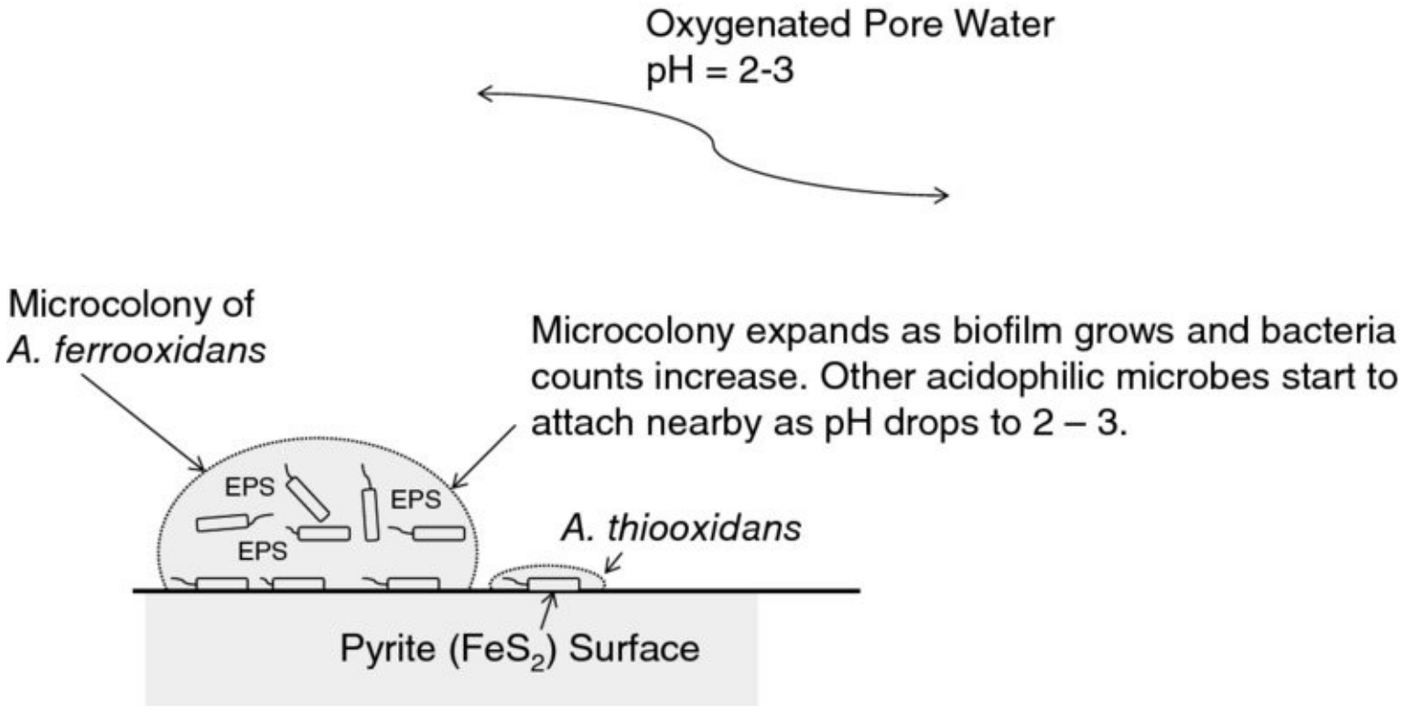


FIGURE 3.27 Step 3: Microcolonies of *A. ferrooxidans* develop, biofilm formation begins, and the pH in the pore water drops. Not to scale.

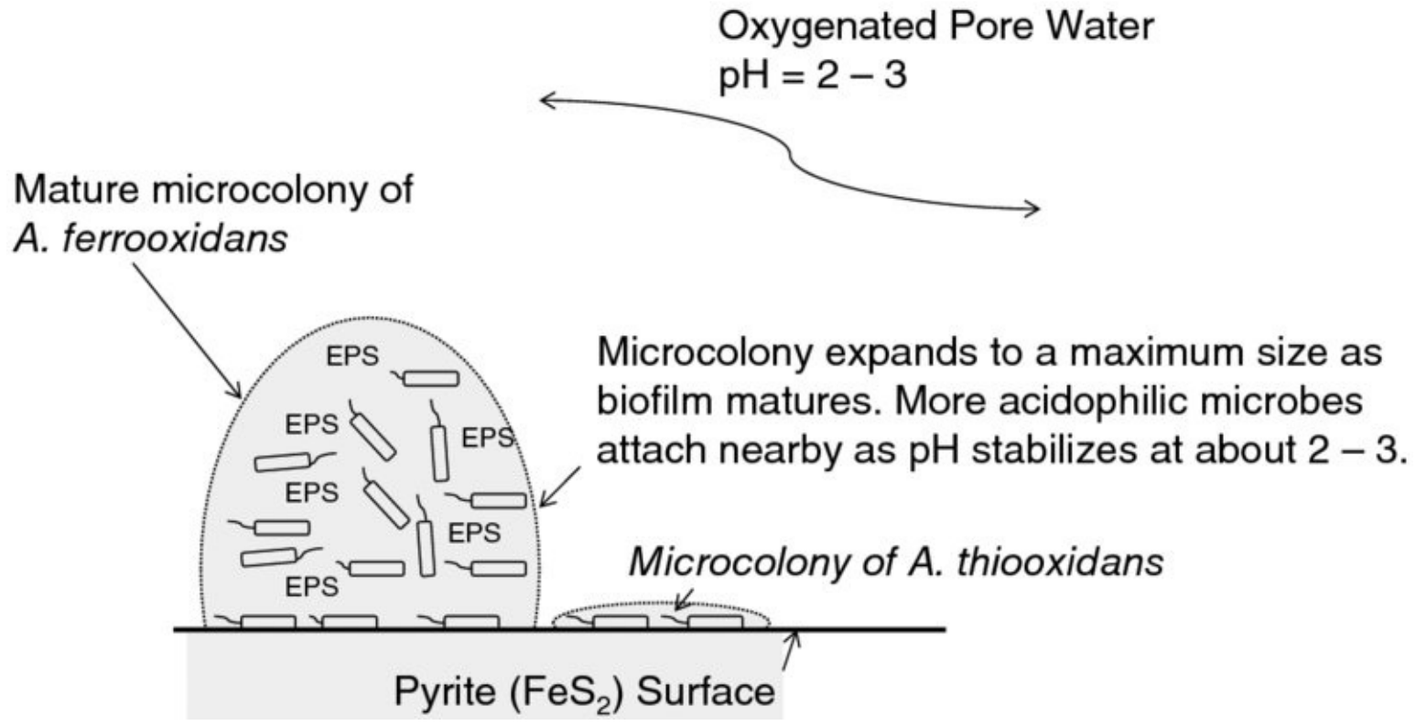


FIGURE 3.28 Step 4: Microcolonies of *A. ferrooxidans* expand, biofilm formation matures, and the pH in the pore water stabilizes. Not to scale.

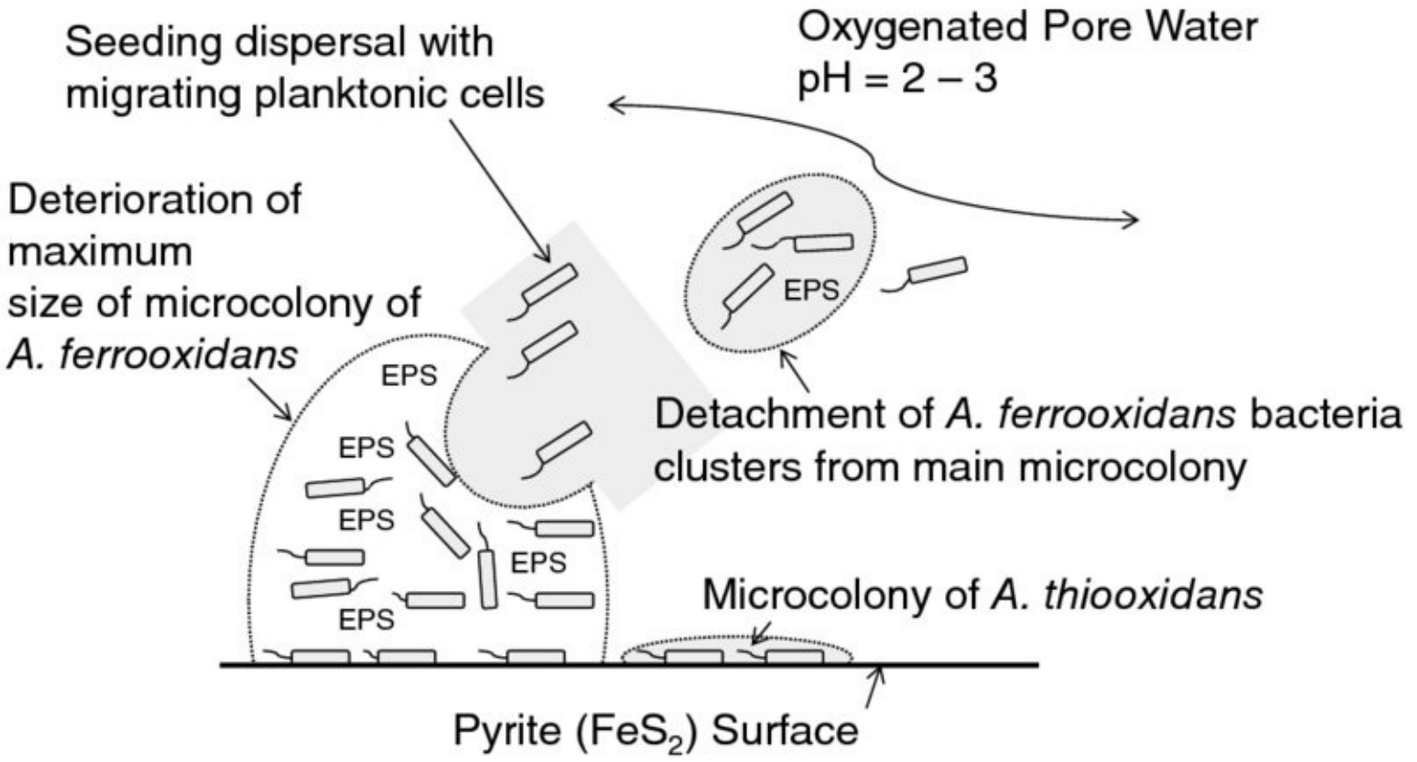


FIGURE 3.29 Step 5: Bacteria clusters detach from the main microcolony. Not to scale.

Colonization of Pyrite

The origin of acidity for acid drainage was described in a study by Mielke et al. (2003). In the study it was noted that *A. ferrooxidans* not only survives at a pH value of 7 in a simulated sulfide-rich tailings setting but was able to begin the oxidation of pyrite at neutral pH. Localized acidification occurred within just 14 days of colonization. It was noted that *A. ferrooxidans* has adapted to a pH value of 2 in pore or surface waters, the outer cell membrane, and even in the periplasm, yet the bacteria maintain a pH value of 7 in the cytoplasm (see Figure 3.17). Within a saturated pore space between pyrite grains, groundwater prior to acidification commonly has a pH value of 6 to 8.

Importance of Microbial Participation in Sulfide Oxidation

Since the iron- and sulfide-oxidizing microbes are acidophilic chemolithotrophic organisms, there is likely to be little bacterial participation in pyrite oxidation at neutral to alkaline pH. Evangelou (1995, 1998) noted the mechanisms of pyrite oxidation by iron-oxidizing bacteria as being either direct or indirect metabolic reactions. Direct metabolic reactions require physical contact between the bacteria and pyrite particles; indirect metabolic reactions do not require physical contact. During indirect metabolic reactions, the bacteria oxidize Fe^{2+}, which regenerates the Fe^{3+} required for the chemical oxidation of pyrite (Singer and Stumm, 1970). The ferric iron can also react directly with the pyrite and act as a catalyst in generating much greater amounts of ferrous iron, sulfate, and additional acidity. Reaction (3.9) shows that Fe^{3+} and O_2 are the major pyrite oxidants, and (3.10) shows the reaction of the ferric iron (Fe^{3+}) with the pyrite (FeS_2) in the presence of water to form the soluble iron (Fe^{2+}) ion and sulfate (SO_4^{2-}) ion in solution. The excess H^+ ions add to a lower pH value and reflect an acidic environment.

When ferrous iron is produced [reaction (3.10)] and sufficient dissolved oxygen is present, the cycle of reactions shown in (3.8) and (3.9) are perpetuated (Younger et al., 2002). Without dissolved oxygen,

(3.11) will continue to completion and water will show elevated levels of ferrous iron (Younger et al., 2002). The rates of chemical reactions [(3.5) to (3.7)] can be accelerated significantly by iron- or sulfide-oxidizing microbes, and in the past two decades, specific microbes have been identified in the literature, such as *Thiobacillus ferrooxidans*. Another microbe, *Ferroplasma acidarmanus*, has been identified in sulfuric acid production in mine waters (McGuire et al., 2001). Based on recent DNA evidence and more phylogenetic research, it now appears that various lithotrophic iron- and sulfide-oxidizing microorganisms with similar characteristics catalyze the pyrite oxidation reaction as part of their cellular respiration processes. These acidophilic microbes (mostly bacteria and archaea) comprise a wide diversity in both physiology and phylogeny. These microbe-catalyzed reactions, (3.9) to (3.11), commonly occur where acidic waters with substantial dissolved metals blend with cleaner waters, resulting in the precipitation of metal hydroxides on stream channel substrates (Jennings et al., 2008).

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_{3(s)} + 3H^+ \tag{3.9}$$

$$Fe^{2+} + \tfrac{1}{4}O_2 + 2\tfrac{1}{2}H_2O \rightleftharpoons Fe(OH)_{3(s)} + 2H^+ \tag{3.10}$$

$$Mn^{2+} + \tfrac{1}{4}O_2 + 2\tfrac{1}{2}H_2O \rightleftharpoons Mn(OH)_{3(s)} + 2H^+ \tag{3.11}$$

Other metal sulfide minerals in addition to pyrite may be associated with economic ore deposits, and some of these minerals may also produce acidity and SO_4^{2-}. Oxidation and hydrolysis of the metal sulfide minerals pyrrhotite ($Fe_{1-x}S$), chalcopyrite ($CuFeS_2$), sphalerite [(Zn,Fe)S], and others can mobilize metals such as zinc, lead, nickel, and copper into solution in addition to producing acidity and SO_4^{2-} (Younger et al., 2002; Jennings et al., 2008).

Biogeochemical Limiting Factors

If any of the processes represented by the reactions shown earlier were slowed or halted, the generation of sulfuric acid drainage would also slow or cease (Mills, 1995a,b). Removing contact with atmospheric oxygen or water with adequate dissolved oxygen from the acid generation area would cause two of the three main reactants, water and oxygen, not to be present. Therefore, the aerobic bacteria that oxidize iron or sulfides will not oxidize iron sulfides in the absence of oxygen and water. Water in the form of vapor or moisture may be enough to start the pyrite-oxidizing process. The removal of oxygen and water from the area containing reduced iron sulfides would stop pyrite from being oxidized. Almost complete absence of oxygen occurs in nature when pyrite is found beneath the water table, where aerobic oxidizing conditions are limited largely by the approximate 8 mg/L solubility limit at oxygen in water. Under these conditions, the pyrite remains almost completely unreacted and in a reduced state. In the absence of dissolved oxygen, microbial communities in anaerobic environments rely primarily (in order of decreasing energy potential) on nitrate (NO_3^-), manganese(IV), iron(III), sulfate (SO_4^{2-}), and finally, carbon dioxide (CO_2) as their main energy source, also called *terminal electron acceptors*.

When pyrite is enclosed within massive rock, only minimal amounts of pyrite are oxidized through natural weathering, thereby generating only small amounts of acid, and this acid is sometimes naturally diluted or neutralized by surrounding alkaline rocks such as carbonates. Coal seams frequently occur in the vicinity of deposits of limestones and dolomites. However, when large volumes of pyritic material are fractured and exposed to oxidizing conditions, which can occur in mining or other major land disturbances, the pyrite reacts, and water dissolves and moves the reaction products (Fe and other metals, sulfate, and acidity) into groundwater and surface water sources.

Microbial Reactions

Abiotic oxidation of Fe^{2+} with O_2 is extremely pH sensitive, and the abiotic reaction is rapid above pH 5 and becomes extremely slow in a very acidic solution (Evangelou, 1998). Unfortunately, in contrast, in the presence of the ubiquitous iron- and sulfide-oxidizing microbes, Fe^{2+} oxidation is extremely rapid in acid solutions, lowering the pH and increasing the metal mobility.

Pyrite oxidation chemistry is complex, and some researchers have noted chemical stoichiometry of sulfuric acid generation with microbial processes. It is established that the iron- and sulfide-oxidizing microbes catalyze the reactions and are an integral part of the geochemical stoichiometry [reactions (3.12) to (3.17)] (Mills, 1995b; Shaw and Mills, 2000). The iron-oxidizing bacteria are ubiquitous. Reactions (13.12) to (13.17) describe the oxidation of pyrite (FeS_2) to the products that constitute the contaminants generically termed acid rock drainage, although similar reactions may be written for the oxidation of pyrrhotite (FeS). Iron- and sulfide-oxidizing microbes greatly accelerate the reactions shown.

$$FeS_2 + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + 2S \tag{3.12}$$

$$4Fe^{2+}_{(aq)} + O_{2(g\ or\ aq)} + 4H^{+}_{(aq)} + \text{iron-oxidizing bacteria} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O \tag{3.13}$$

$$4FeSO_4 + O_2 + 2H_2SO_4 + \text{iron-oxidizing bacteria} \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \tag{3.14}$$

$$2S + 3O_2 + 2H_2O + \text{iron-oxidizing bacteria} \rightarrow 2H_2SO_4 \tag{3.15}$$

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4 \tag{3.16}$$

$$S^0 + 3Fe_2(SO_4)_3 + 4H_2O \rightarrow 6FeSO_4 + 4H_2SO_4 \tag{3.17}$$

Acid Drainage Biogeochemistry of Some Specific Minerals

In hardrock mining areas, metallic minerals containing sulfur are common. Galena [i.e., lead sulfide (PbS)], chalcopyrite [i.e., iron–copper sulfide (FeS·CuS)], sphalerite [i.e., zinc sulfide (ZnS)], in addition to pyrite and pyrrhotite, are commonly present in hardrock mining areas. In those cases, a secondary acidifying effect of the oxidation of the iron–sulfur minerals to sulfuric acid and ferric iron may be observed (Mills, 1995b). The stable pH developed (2.5 to 3.0) and the products of sulfuric acid and ferric sulfate create conditions where the Fe^{3+} ion itself can act as an oxidant in the acid generation process. Above about pH 3, the ferric ion is itself hydrolyzed to ferric hydroxide, which precipitates as the familiar bright yellow to orange rust-colored stains found in creek beds and associated with acid drainage. The ferric hydroxide is commonly called “yellow boy.” In the absence of ferric iron at pH 2.5 to 3.0, sulfuric acid will dissolve some heavy metal carbonate and oxide minerals but has little reactive effect on heavy metal sulfides. However, the ferric iron ion is capable of dissolving many heavy metal sulfide minerals, including those of lead, copper, zinc, and cadmium, by the general reaction (Mills, 1995b)

$$MS + nFe^{3+} = M^{n+} + S + nFe^{2+} \tag{3.18}$$

where MS is solid heavy metal sulfide, Fe^{3+} is an aqueous ferric iron ion, M^{n+} is an aqueous heavy metal ion, S is sulfur, and Fe^{2+} is an aqueous ferrous iron ion.

It is by this acid generation process that significant amounts of heavy metals become solubilized. Many metallic elements, arsenic being one of the most toxic, are often present at trace levels within the minerals pyrite and pyrrhotite. Oxidation of these minerals can therefore release and mobilize these trace elements, creating metal contamination and environmental damage far beyond the initial lowering pH by sulfuric acid generation.

Neutralization of the acidic metal-rich solutions that can be generated by the chemical reactions shown earlier may also occur as a result of dissolution of neutralizing minerals, such as carbonates, that come in contact with acidic solutions. Examples of these reactions (Shaw and Mills, 2000)

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \quad (3.19)$$

calcite dissolution by sulfuric acid

$$CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow CaSO_4 + MgSO_4 + 2H_2O + 2CO_2 \quad (3.20)$$

dolomite dissolution by sulfuric acid (3.20)

Note that both of these carbonate reactions also produce carbon dioxide, which is essential for, and a stimulant to, carbon dioxide–consuming autotrophic microbes.

Reactions of other waste rocks associated with hardrock mining [(3.21) to (3.26)] may also contribute to secondary chemical reactions and dissolution of particular minerals in areas of potential acid drainage generation under specific pH conditions. The simplified reactions shown below are the generalized reactions that take place as starting and end products. In actuality, there are series of intermediation reactions and reaction products. The overall process is complex and involves both abiotic and biotic transformations.

$$KAl_2[AlSi_3O_{10}](OH)_{2(s)} + H^+ + \tfrac{3}{2}H_2O \rightarrow K^+ + \tfrac{3}{2}Al_2Si_2O_5(OH)_{4(s)} \quad (3.21)$$

muscovite dissolution

$$KMg_{1.5}Fe_{1.5}AlSi_3O_{10}(OH)_{2(s)} + 7H^+ + \tfrac{1}{2}H_2O \rightarrow K^+ + \tfrac{3}{2}Mg^{2+} + \tfrac{3}{2}Fe^{2+} + H_4SiO_4^0 + \tfrac{1}{2}Al_2Si_2O_5(OH)_{4(s)} + 2O_{2(g)} + H_{2(g)} \quad (3.22)$$

biotite dissolution

$$NaAlSi_3O_{8(s)} + H^+ + \tfrac{9}{2}H_2O \rightarrow Na^+ + 2H_4SiO_4^0 + \tfrac{1}{2}Al_2Si_2O_5(OH)_{4(s)} \quad (3.23)$$

albite dissolution

$$CaAl_2Si_2O_{8(s)} + 2H^+ + H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_{4(s)} \quad (3.24)$$

anorthite dissolution

$$KAlSi_3O_{8(s)} + H^+ + \tfrac{9}{2}H_2O \rightarrow K^+ + 2H_4SiO_4^0 + \tfrac{1}{2}Al_2Si_2O_5(OH)_{4(s)} + 2O_{2(g)} + H_{2(g)} \quad (3.25)$$

K-feldspar dissolution

$$Fe(OH)_{3(s)} + 3H^+ \rightarrow Fe^{3+} + 3H_2O \quad (3.26)$$

iron-oxyhydroxide dissolution

Aluminum Reactions

Aluminum is a metal commonly released from a rock or soil matrix that can also hydrolyze to release acidity. Reactions (3.27) to (3.29) proceed stepwise to release, overall, 3 mol of acidity (Thomas et al., 2003). Aluminum ions (Al^{3+}) exist at low pH and are very toxic to plants and marine organisms.

$$Al^{3+}_{(aq)} + H_2O \rightarrow Al(OH)^{2+}_{(aq)} + H^+_{(aq)} \quad (3.27)$$

$$Al(OH)^{2+}_{(aq)} + H_2O \rightarrow Al(OH)^{2+}_{(aq)} + H^+_{(aq)} \quad (3.28)$$

$$Al(OH)^{2+}_{(aq)} + 2H_2O \rightarrow Al(OH)^{3+}_{(aq)} + 2H^+_{(aq)} \quad (3.29)$$

Manganese and Iron Oxides

Ferric iron (Fe^{3+}) is a major oxidant of pyrite regardless of pH (Evangelou, 1998). Ferrous iron (Fe^{2+}) can oxidize in the presence of manganese oxides (Asghar and Kanehiorn, 1981) as noted in (3.30). The dissolution of ferric iron (Fe^{3+}) minerals such as goethite (FeOOH) leads to aqueous ferric iron complexes, as shown in (3.28) (Evangelou, 1998). The reaction represents the dissolution of ferric iron minerals by organic ligands, which are weak-field organic acids produced on or near the surface by plants and microbes and generally contain oxygen as hydroxyl or carboxyl functional groups (Hider, 1984). Pyritic mine waste and coal residues are known to contain manganese oxides and iron oxides (Barnhisel and Massey, 1969). Ferric iron produced through either of the reactions

$$MnO_2 + 4H^+ + 2Fe^{2+} \rightleftharpoons Mn^{2+} + 2H_2O + 2Fe^{3+} \quad (3.30)$$

$$FeOOH + 3H^+ + \text{ligand} \rightarrow Fe^{3+} - \text{ligand} + OH^- \quad (3.31)$$

may oxidize pyrite (Luther et al., 1992).

Pyrite Oxidation Rates

Pyrite oxidation reaction rates vary, based on numerous site-specific geochemical conditions. The rate of pyrite oxidation depends on numerous variables, such as:

- Reactive surface area of pyrite (Singer and Stumm, 1968, 1970)
- Form of pyritic sulfur (Caruccio et al., 1988)
- Oxygen concentrations (Smith and Shumate, 1970)
- Solution pH (Smith and Shumate, 1970)
- Catalytic agents (Caruccio et al., 1988)
- Flushing frequencies (Caruccio et al., 1988)
- The presence of iron-oxidizing bacteria (U.S. Environmental Protection Agency, 1971)

Microbial Control

The iron-oxidizing bacteria serve as a reaction catalyst and are crucial for the generation of most acid mine drainage (Waksman, 1922; Leathen et al., 1953). In coal mine environments where bacterial activity determines the rate of acid generation, inhibition of iron-oxidizing bacteria can prevent acidification or at least greatly reduce the acidity that is produced. The concept of developing and applying bactericides to kill iron-oxidizing microbes was considered originally in 1953 but was rejected as probably impractical (Leathen, 1976). Several unsuccessful attempts to develop bactericides followed in the ensuing years (Barnes and Romberger, 1968; Shrearer et al., 1970). Bactericidal control of acid drainage was developed and used to kill the iron-oxidizing microbes over a decade later (Kleinmann, 1979; Kleinmann and Erickson, 1981). According to Kleinmann (1988), anionic surfactants have proven to be cost-effective to directly inhibit the iron-oxidizing bacteria that catalyze acid generation when applied directly to highly pyritic material. Controlled time release of surfactants is used appropriately just before the pyritic material, usually mine waste rock, is buried and covered with nonpyritic material during site restoration and revegetation.

Oxygen may be the rate-limiting step in mine waste tailing piles or dredge spoil piles of low porosity and permeability such as that composed of soft shale or clays, so that oxidation is limited to the upper few meters of stock piles. In porous and permeable spoils composed of coarse sands, gravels, or broken rock fragments consisting of conglomerates or coarse sandstone, air convection driven by the heat generated by pyrite oxidation may provide large amounts of oxygen deep into the spoil piles (Guo et al., 1994; Guo and Cravotta, 1996).

Review of Naturally Occurring Acid Drainage

In nature, the neutralization of acid rock drainage, either in situ or at some distance from the source of acid generation, results in a different rock or sediment geochemistry as well as a different appearance. In these cases, the rocks, sediments, or soils appear to be oxidized and differ in texture and color from the host source material. Mining geologists have used field observations of natural acid drainage as an aid in mineral exploration. The oxidized rocks, called *gossans* and sediment chemistry are indicative of potential mineral deposits. Gossans have been a target of mineral prospectors and are easily identified in the field, as they are generally reddish brown to yellow-ochre in color. There are many examples of locating gossans which lead to the discovery of major ore bodies and to important economic mining operations (Mills, 1995b).

Economic mineral deposits such as bauxite, the ore of aluminum, laterite, the ore of nickel, and supergene oxide zones that may contain economic deposits of copper, gold, and silver are products of natural acid rock generation developed over several thousand years. The mineral ores are derived from the breakdown of minerals, which may occur in several rock types at the surface. Minerals are also formed as a result of acid rock drainage processes. Some of these minerals, such as boleite, are rare and highly prized by mineral collectors. Other minerals, such as malachite, are used for jewelry, and some of these minerals, such as chalcocite, form other types of deposits (Mills, 1995b).

Geochemistry in Perspective

Pyrite, iron sulfides, and other oxygen-sensitive minerals, such as siderite (iron carbonate; $FeCO_3$) and uraninite (uranium dioxide; UO_2), are oxygen-sensitive minerals. As such, their presence in the rock

record indicates the oxidizing potential of the oxygen in the atmosphere and water bodies at the time of deposition. Putting the geochemistry of the acid generation process into perspective is important. The geochemical process of oxidizing iron sulfide minerals has been occurring on Earth for 2.2 to 2.3 billion years, when free oxygen in the air and surface waters and ocean was small and probably reached up to 1% of the 20.9% oxygen measured in the current atmosphere. Before 2.2 to 2.3 billion years ago, pyrite crystals were found in surficial sedimentary rock deposits, indicating that pyrite and other iron sulfide minerals were deposited at a time when the atmosphere was virtually devoid of oxygen. Since that time, sulfuric acid generation from pyrite oxidation has been occurring naturally on Earth as iron sulfide minerals have been weathered and eroded (Knoll, 2003).

Anthropogenic disturbance of surface rock, sediments, and soils containing iron sulfide by early metal mining activities, about 2000 years ago, has started the same acid drainage geochemical processes. Acidic drainage has been identified as the largest environmental liability facing the mining industry on a worldwide basis. One of the largest problems is historic and abandoned mining operations in which the acid drainage process has started and no responsible funding source is available for acid mine drainage mitigation and site cleanup and restoration. Once started, the acid generation process is virtually impossible to stop without a significant effort to remove the sources of oxygen and water, due to the iron-oxidizing bacteria, which act as catalysts. Acid generation does not stop due to the length of time since the iron sulfides were first exposed to oxygen. It has been documented that at some Roman mine sites, acid generation has remained active for over 15 centuries. Acid mine drainage continues to emanate from mines in Europe established during the Roman Empire, prior to A.D. 467 (Center for Streamside Studies, 2002).

Preventing Aerobic Respiration: AMD Control

Acid mine drainage prevention and remediation options have been summarized by Johnson and Hallberg (2005). Since both oxygen and water are required to generate soluble metals and sulfuric acid, excluding either oxygen or water or both should be a way to stop or minimize acid drainage by limiting cellular respiration of the aerobic microbial communities that oxidize iron and sulfide minerals. Excluding water and oxygen in underground mines requires a detailed location of all faults, joints, fractures, surface conduits, shafts, and adits. It is important that this includes locations where the influx of rainwater or groundwater containing dissolved oxygen does not occur (Johnson and Hallberg, 2005). Many mines extend below the shallow groundwater, and when mine pumps are finally turned off during mine abandonment, the natural groundwater elevation is likely to rebound, changing such geochemistry conditions as pH and redox in the mine and surrounding subsurface. These geochemical changes need to be evaluated for acid generation and heavy metal mobilization potential.

For acid drainage prevention, methods include flooding or sealing of underground mines to prevent oxygen and water from coming in contact with the microbial communities that can live on iron sulfide mineral surfaces. Surface water normally has about 8 mg/L dissolved oxygen. Dissolved oxygen content can be reduced in water by mixing in carbon-rich organic material that ferments over time, creating temporary anaerobic conditions. Sludge from water treatment plants, high in biological oxygen demand, have been used to lower dissolved oxygen levels in mine waters. The anaerobic conditions in the water last as long as there are carbon substrates and other terminal electron acceptors available in the absence of dissolved oxygen. Once the dissolved oxygen becomes available in water, pyrite oxidation and acid generation will restart.

Underwater storage of mine tailings can be improved by covering with a layer of clay or organic-rich material, by land-based storage in sealed waste heaps, by blending of mineral wastes to lower acid

drainage potential by mixing acid-generating rocks with acid-consuming media, and by total solidification of tailings using soluble phosphates with hydrogen peroxide to coat or armor pyrite-rich rocks. The application of anionic surfactants to tailing piles as biocides has been described by Kleinmann et al. (1998) and Kleinmann (2000). Microencapsulation by coating reactive surfaces has also been tried in the field. Preventing acid drainage once land disturbance has occurred and pyrite surfaces are exposed to oxygen in air and water is technically difficult. Therefore, the best preventive method for acid mine drainage, acid rock drainage, and acid sulfate soils is planning field activities to minimize the disturbance of land containing pyrite-rich rocks during mining or property development, and to divert water away from acid source media when possible.

Summary

The geologic history of oxygen, sulfur, and iron on the Earth reflects the importance of redox reactions. The biogeochemistry of the oceans and other water bodies and the mix of gases in the atmosphere has changed significantly over time (Cloud, 1983a,b). Accounting for 88% of geologic time, the Precambrian spans from 4.6 billion years ago (BYA) to about 0.541 BYA. The earliest atmosphere would have had hydrogen, helium, and other hydrogen-containing gases. These light gases would have been lost fairly quickly due to the radiation from the sun, creating an early rocky planet devoid of an atmosphere. The first atmosphere created by the Earth was formed by the release of gases trapped in its interior through volcanic processes, and was likely dominated by water vapor. As the surface temperature dropped, water vapor turned to rain, forming the oceans. The global filling of the ocean basins would have further reduced atmospheric concentrations of CO_2, which is highly soluble in water. At this point, the atmosphere was dominated by nitrogen, but no free oxygen existed. Without any free oxygen, ferrous iron, pyrite, or other sulfur minerals on the surface of the Earth would have remained in a reduced state. Although variations exist, early volcanic off gassing created an atmosphere that was probably about 95 to 97% water vapor, 1 to 2% carbon dioxide, 1 to 3% silicon dioxide, with minor to trace percentages of the remaining gases. The early atmosphere may be similar to the description of Momotombo, an active volcano in Nicaragua on a convergent plate boundary. A study (Symonds et. al., 1994) showed that volcanic gases from Momotombo contained H_2O (97.1%), CO_2 (1.44%), SO_2 (0.50%), H_2 (0.70%), CO (0.01%), H_2S (0.23%), HCl (2.89%), and HF (0.26%). Free oxygen is absent, and is not a component of past or current volcanoes. Current atmospheric concentration of oxygen is 20.95% and surface waters at sea level at about 10°C (50°F) have a dissolved oxygen content of about 8 mg/L or parts per million and these geochemical conditions impact microbial processes. By comparison, the atmosphere on Earth today contains N_2 (78.09%), O_2 (20.95%), Ar (0.93%), CO_2 (0.039%) and less than 0.002% of Ne, He, and CH_4 (U.S. Standard Atmosphere, 1976).

Upon the cessation of ocean-evaporating asteroid strikes, called the late heavy bombardment at the end of the Hadean about 4 BYA, anaerobic microbial life started approximately 3.8 BYA or earlier, and it was firmly established by 3.5 BYA where water bodies were reducing zones containing little to no molecular oxygen (O_2). The atmosphere also contained no free oxygen. With the evolution of oxygenic photosynthetic microbes, such as cyanobacteria, oxygen was produced as a byproduct of photosynthesis:

$$6CO_2 + 6H_2O\,(\text{with Sun's energy and Chlorophyll}) \rightarrow C_6H_{12}O_6\,(\text{sugars}) + O_2$$

The microbial generation of free oxygen in the atmosphere started about 3 BYA to about 2.6 BYA. Microbial aerobic metabolism was more efficient than anaerobic pathways, and the presence of oxygen

created new ecosystem opportunities. Reflecting the enormous redox buffering capacity on the surface of the early Earth, produced oxygen began to accumulate slowly over time, changing the geochemistry of the atmosphere and oceans. At this time, nonmarine pyrite-rich sediments deposited in an oxygen-free atmosphere would have been preserved as pyrite, an indicator that free oxygen did not exist to oxidize the sulfide minerals. Iron, exposed to air, did not rust or oxidize in the early pre-oxygen Earth atmosphere. As more oxygen was generated, common reduced species, such as ferrous iron, hydrogen sulfide, and methane, reacted with free oxygen for billions of years until those reduced minerals were fully oxidized. About 2.4 BYA, the biologically induced appearance of free oxygen (O_2) in the atmosphere was marked by the Great Oxygenation Event (GOE), which relates directly to the potential for global oxidation of pyrite exposed to the atmosphere or in oxygenated waters, and the start of the sulfuric acid generation processes. Evidence for dating the GOE relates to the way sulfur dioxide gas is chemically broken down or reduced in the atmosphere. In an oxygen-free atmosphere, the breakdown of sulfur dioxide by sunlight produces a distinctive mixture of sulfur isotopes that is independent of their weight. If free oxygen is present in the atmosphere, a different, weight-dependent mixture is produced. Each of these isotope mixtures is preserved in sulfur-bearing minerals, such as pyrite in sedimentary rocks. Extensive sampling of sedimentary rocks first revealed that the mixture of sulfur isotopes produced by an oxygen-free atmosphere disappeared after 2.4 BYA. However, more recent studies of Achaean rocks from Western Australia revealed the possibility of oxygen in the atmosphere before that date. Whatever the final outcome of this controversy, the amount of oxygen in the early atmosphere was still perhaps 5–10 times less than today. The Precambrian atmosphere (Lindsey et al., 2007) did not have as much oxygen as today, but by 2.2 BYA it had access to aerobic microbial communities with just enough oxygen to rust iron and oxidize pyrite, the source of acid drainage. Once free oxygen had accumulated in the atmosphere and dissolved oxygen was present as dissolved oxygen in water bodies, sulfuric acid generated from aerobic microbial colonization on the surfaces of pyrite and other reduced sulfide minerals was firmly established.

Other major geochemical changes occurred during the Precambrian. The Precambrian included evidence of the oldest glaciation at about 2.9 billion years ago from rocks in South Africa. The oldest widespread glaciers were found in Huronian rocks of Ontario from 2.2 to 2.4 billion years ago. Other Precambrian glaciations occurred from about 0.750 to 0.580 BYA near the end of the Precambrian. The biogeochemical interaction of microbes and oxygen with freshly exposed pyrite-rich rocks or sediments – caused by retreating Precambrian glaciers during these glaciation periods – would have created acid drainage similar to what is observed in the Andes Mountains of today, where mountain glaciers are melting, exposing pyrite and creating acidic drainage. Fluctuating temperatures occurred during the Precambrian, reflecting major changes in atmospheric composition related to volcanic off gassing and to microbial production of oxygen and other gases. Deposition of carbonate rocks in the vicinity of the some Precambrian glacial sediments were evidence of rapid warming temperatures (Lindsey, 2007). Other indicators of major changes in global ocean and atmospheric geochemistry during the Precambrian are reflected in the banded iron formations (BIF) and red bed deposition.

Oxygen in the atmosphere did not approach modern levels until 0.600 to 0.700 BYA. Oxygen in the atmosphere began to accumulate to significant levels of about 15% to 20% at the start of the Cambrian about 0.542 BYA. The explosion of complex multicellular life at this time was the biological response to the enormous accumulation of oxygen produced from microbial processes. There were changes in carbon dioxide and oxygen as well, since the Cambrian explosion have likely had observable effects on acid generation on the Earth. Higher concentrations of CO_2 in the atmosphere and in water would have increased karstification processes and may have encouraged autotrophic organisms, including plants, to synthesize more biomass. During the main coal-forming Carboniferous period, atmospheric oxygen levels

reached a maximum of 35% by volume centered around 0.300 BYA (Berner, 2006; Berner et al., 2007; Berner and Canfield, 1989). At the same time, surface waters would have had a dissolved oxygen content of about 13.4 mg/L. The higher levels of oxygen in the atmosphere, soil pore spaces, and in surface water may have created deeper aerobic zones for sulfide oxidation.

Today some of the highest incidences of acid drainage occur at the countless abandoned mine sites throughout the world and at operational mines where sulfide oxidation mitigation measures have failed to prevent the release of acid drainage to downgradient surface waters. The resulting low-pH conditions that accompany the generation of sulfuric acid mobilize metals from pyrite-rich rocks, sediments or soils, resulting in degradation of water quality and the environment (Jennings et al., 2008; Neuman et al., 2009). Although not all mines or mining activities produce acid drainage, without proper assessment, monitoring, and mitigation, mining and construction activities in areas with sulfide-rich rocks and soils can generate acid drainage. Understanding the key biogeochemical factors for microbial success allows for manipulation and optimization of environmental conditions in bioleaching mining techniques. In this mining technique, environmental conditions are optimized and monitored to allow microbial processing of mineral wastes to extract valuable metal ores. Minimizing acid drainage requires an understanding of ancient redox reactions and eliminating favorable environmental conditions conducive to the robust growth of iron- and sulfur-oxidizing microbial communities.

References and Suggested Reading

Agricola, G., 1556. *De Re Metallica*. Translated in 1912 by H.C. Hoover, and L.H. Hoover. Republished by Dover, New York, 1950, 572 pp.

Ahern, C.R., McElnea, A.E., and Sullivan, L.A., 2004. Acid sulfate soils laboratory methods guidelines. In: Queensland Acid Sulfate Soils Manual 2004. Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia, 186 pp.

American Society for Testing and Materials, ASTM, 1995. Standard Test Methods for Low-Level Dissolved Oxygen in Water. ASTM D5543-94. Philadelphia, PA.

Andreae, M.O., and Rosenfeld, D., 2008. Aerosol–cloud–precipitation interactions: 1. The nature and sources of cloud-active aerosols. Earth Science Reviews, vol. 89, pp. 13–41. doi: 10.1016/j.earscirev.2008.03.001.

Apel, W.A., Dugan, P.R., and Tuttle, J.H., 1980. 5′-Triphosphate formation in *Thiobacillus ferrooxidans* vesicles by H^+ ion gradients comparable to those of environmental conditions. Journal of Bacteriology, vol. 142, pp. 295–301.

Asghar, M., and Kanehiorn, Y., 1981. The fate of applied iron and manganese in an oxisol and an ultrasol from Hawaii. Soil Science, vol. 131, pp. 53–55.

Baker, B.J., and Banfield, J.F., 2003. Microbial communities in acid mine drainage. FEMS Microbiology Ecology, vol. 44, pp. 139–152.

Baker, B.J., Lutz, M.A., Dawson, S.C., Bond, P.L., and Banfield, J.F., 2004. Metabolically active eukaryotic communities in extremely acidic mine drainage. Applied and Environmental Microbiology, vol. 70, no. 10, pp. 6264–6271.

Baker-Austin, C., and Dopson, M., 2007. Life in acid: pH homeostasis in acidophiles. Trends in

Microbiology, vol. 15, pp. 165–170.

Barnes, H.L., and Romberger, S.B., 1968. Chemical aspects of acid mine drainage. Journal of the Water Pollution Control Federation, vol. 40, pp. 370–384.

Barnhisel, R.I., and Massey, H.F., 1969. Chemical, mineralogical and physical properties of eastern Kentucky acid-forming coal spoil materials. Soil Science; vol. 108, pp. 367–372.

Berner, R.A., and Canfield, D.E., 1989. A new model for atmospheric oxygen over Phanerozoic time. American Journal of Science, vol. 289, pp. 333–361.

Berner, R.A., 2006. GEOCARBSULF: A combined model for Phanerozoic atmospheric O_2 and CO_2. Geochmica et Cosmochimica Acta, vol. 70, pp. 5653–5664.

Berner, R.A., VandenBrooks, J.M., and Ward, P.D. 2007. Oxygen and evolution. Science, vol. 316, pp. 557–558.

Bonev, I.K., Reiche, M., and Mannov, M., 1985. Morphology, perfection and growth of natural pyrite whiskers and thin platelets. Physics and Chemistry of Minerals, vol. 12, pp. 223–232.

Brady, K.B., Shaulis, J.R., and Sekma, V.W., 1988. A study of mine drainage quality and prediction using overburden analysis and paleoenvironmental reconstructions, Fayette County, Pennsylvania. In: Conference Proceedings, Mine Drainage and Surface Mine Reclamation. Information Circular 9183. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 33–44.

Brady, K.B.C., Smith, M.W., and Schueck, J., 1998. Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection, Harrisburg, PA.

Brimblecombe, P., 2003. The global sulfur cycle. In: Treatise on Geochemistry, vol. 8, H.D. Holland, and K.K. Turekian, eds. Elsevier, New York, pp. 645–686.

Brown, C.J., Rakovan, J., and Schoonen, M.A.A., 2000. Heavy Minerals and Sedimentary Organic Matter in Pleistocene and Cretaceous Sediments on Long Island, New York, with Emphasis on Pyrite and Marcasite in the Magothy Aquifer. U.S. Geological Survey, Water-Resources Investigations Report 99-4216. Prepared in cooperation with the Suffolk County Water Authority, Coram, NY, 22 pp.

Brydie, J.R., Wogelius, R.A., Merrifield, C.M., Boult, S., Gilbert, P., Allison, D., and Vaughan, D.J., 2004. The µ2M project on quantifying the effects of biofilm growth on hydraulic properties of natural porous media and on sorption equilibria: an overview. In: Understanding the Micro to Macro Behavior of Rock–Fluid Systems, R.P. Shaw, ed. Special Publication 249. Geological Society Publishing House, Bath, UK, pp. 131–144.

Brydie, J.R., Wogelius, R.A., Boult, S., Merrifield, C.M., and Vaughan, D.J., 2009. Model system studies of the influence of bacterial biofilm formation on mineral surface reactivity. Biofouling (Alberta Research Council, Edmonton, AB, Canada), vol. 25, no. 5, pp. 463–472.

Buerger, M.J., 1931. The crystal structure of marcasite. American Mineralogist, vol. 16, pp. 361–395.

Canfield, D.E., and Farquhar, J., 2012. The global sulfur cycle. In: Fundamentals of Geobiology, A.H. Knoll, D.E. Canfield, and K.O. Konhauser, eds. Wiley-Blackwell, Chichester, UK, pp. 49–64.

Caruccio, F.T., Hossner, L.R., and Geidel, G. 1988. Pyritic materials: acid drainage, soil acidity, and

liming. In: Reclamation of Surface-Mined Lands, vol 1. CRC Press, Boca Raton, FL, pp. 159–190.

Center for Streamside Studies, 2002. Environmental Impacts of Hardrock Mining in Eastern Washington. College of Forest Resources and Ocean and Fishery Sciences, University of Washington, Seattle, WA.

Chapelle, F.H., 1993. Ground-water Microbiology and Geochemistry. Wiley, New York, 424 pp.

Church, C.D., Richard, T.W., Alpers, C.N., Rye, R.O., and McCleskey, R.B., 2007. Microbial sulfate reduction and metal attenuation in pH 4 acid mine water. Geochemical Transactions, vol. 8, no. 10, pp. 1–14.

Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in neutral waters. Limnology and Oceanography, vol. 14, pp. 429–437.

Cloud, P., 1983a. The biosphere. Scientific American, vol. 249(3), pp. 176–189.

Cloud, P., 1983b. Early biogeologic history: The emergence of a paradigm. In: Earth's Earliest Biosphere: Its Origin and Evolution, J. W. Schopf, ed. Princeton University Press, Princeton, NJ, pp. 14–31.

Colmer, A.R., Temple, K.L., and Hinkle, M.E., 1950. An iron-oxidizing bacterium from the drainage of some bituminous coal mines. Journal of Bacteriology, vol. 59, pp. 317–328.

Department of Environment and Resource Management, 2009. Managing Acid Sulfate Soils. Paper L62. Queensland Government, Queensland, Australia.

Dodony, I., Posfai, M., and Buseck, P.R., 1996. Structural relationship between pyrite and marcasite. American Mineralogist, vol. 81, pp. 119–125.

Donnay, G., Donnay, J.D.H., and Iijima, S., 1977. A high-resolution electron micrograph of the twin boundary in pynte. Acta Crystallographica, vol. A33, pp. 622–662.

Eisler, R., 1988. Lead Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Fish and Wildlife Service Biolog Report 85(1.14). Patuxent Wildlife Research Center, U.S. Fish and Wildlife Service, Laurel, MD.

Emerson, D., and Moyer, C., 1997. Isolation and characterization of novel iron-oxidizing bacteria that grow at circumneutral pH. Applied and Environmental Microbiology, December, pp. 4784–4792.

Evangelou, V.P., 1995. Pyrite Oxidation and Its Control: Acid Mine Drainage, Surface Chemistry, Molecular Oxidation Mechanisms, Microbial Role, Kinetics, Control, Ameliorates, Limitations, Microencapsulation. CRC Press/Lewis Publishers, Boca Raton, FL.

Evangelou, V.P., 1998. Environmental Soil and Water Chemistry: Principles and Applications. CRC Press/Lewis Publishers, Boca Raton, FL, 564 pp.

Fox, G.E., Stackebrandt, E., Hespell, R.B., et al., 1980. The phylogeny of prokaryotes. Science, vol. 209, pp. 457–463.

Gilbert, T.W., Behymer, T.D., and Castaneda, H.B., 1982. Determination of dissolved oxygen in natural and wastewaters. American Laboratory, vol. 14, March, pp. 119–134.

Giovannoni, S.J., and Stingl, U., 2005. Molecular diversity and ecology of microbial plankton. Nature, vol. 437, pp. 343–348.

Gross, S., and Robbins, E.I., 2000. Acidophilic and acid-tolerant fungi and yeasts. Hydrobiologia, vol. 433, pp. 91–109.

Guo, W., and Cravotta, C.A., 1996. Oxygen transport and pyrite oxidation in unsaturated coal-mine spoil. In: Proceedings of the 13th Annual Meeting of the American Society for Surface Mining and Reclamation, Princeton, WV. American Society for Surface Mining and Reclamation, Lexington, KY, pp. 3–14.

Guo, W., Parizek, R.R., and Rose, A.W., 1994. The role of thermal convection in resupplying O_2 to strip coal-mine spoil. Soil Science, vol. 158, pp. 47–55.

Harvey, R.W., George, L.H., Smith, R.L., and LeBlanc, D.R., 1989. Transport of microspheres and indigenous bacteria through a sandy aquifer: results of natural and forced-gradient tracer experiments. Environmental Science and Technology, vol. 23, pp. 51–56.

Heath, R.C., 1983. Basic Ground-water Hydrology. Water Supply Paper 2220, U.S. Geological Survey. Reston, VA, 86 pp.

Hedrich, S., Schlömann, M., and Johnson, D.B., 2011. The iron-oxidizing proteobacteria. Microbiology, vol. 157, no. 6, pp. 1551–1564.

Hider, R.E., 1984. Siderophore mediated absorption of iron. Structural Bonding, vol. 58, pp. 26–87.

Holliger, C., Wohlfarth, G., and Diekert, G., 1998a. Reductive dechlorination in the energy metabolism of anaerobic bacteria. FEMS Microbiology Reviews, vol. 22, pp. 383–398.

Holliger, C., Hahn, D., Harmsen, H., Ludwig, W., Schumacher, W., Tindall, B., Vazquez, F., Weiss, N., and Zehnder, A.J.B., 1998b. *Dehalobacter restrictus* gen. nov. and sp. nov., a strictly anaerobic bacterium that reductively dechlorinates tetra- and trichloroethene in an anaerobic respiration. Archives of Microbiology, vol. 169, pp. 313–321.

Hornberger, R.J., Parizek, R.R., and Williams, E.G., 1981. Delineation of Acid Mine Drainage Potential of Coal-Bearing Strata of the Pottsville and Allegheny Groups in Western Pennsylvania. Research Project Technical Completion Report OWRT Project B-097-PA. Pennsylvania State University, University Park, PA, 359 pp.

Ingledew, W., Cox, J.C., and Halling, P.J., 1977. A proposed mechanism for energy conservation during Fe^{2+} oxidation by Thiobacillus ferro-oxidans: chemiosmotic coupling to net H^+influx. FEMS Microbiology Letters, vol. 2: pp. 193– 197.

Jennings, S.R., Neuman, D.R., and Blicker, P.S., 2008. Acid Mine Drainage and Effects on Fish Health and Ecology: A Review. Reclamation Research Group Publication, Bozeman, MT, 26 pp.

Jiao, Y., D'haeseleer, P., Dill, B.D., Shah, M., Verberkmoes, N.C., Hettich, R.L., Banfield, J.F., and Thelen, M.P., 2011. Identification of biofilm matrix-associated proteins from an acid mine drainage microbial community. Applied Environmental Microbiology, vol. 77, no. 15, pp. 5230–5237.

Johnson, D.B., and Halberg, K.B., 2005. Acid mine drainage remediation options: a review. Science of the Total Environment, vol. 338, pp. 3–14.

Kabata-Pendias, A., 2001. Trace Elements in Soils and Plants, 3rd ed. CRC Press, Boca Raton, FL, 413 pp.

Kelly, D.P., and Wood, A.P., 2000. Reclassification of some species of *Thiobacillus* to the newly designed genera *Acidithiobacillus* gen. nov., *Halothiobacillus* gen. nov. and *Thermithiobacillus* gen. nov., International Journal of Systematic and Evolutionary Microbiology, vol. 50, pp. 511–516.

Keswick, B.H., Wang, D.S., and Gerba, C.P., 1982. The use of microorganisms as ground-water tracers: a review. Ground Water, vol. 20, pp. 142–149.

Kleinmann, R.L.P., 1979. The Biogeochemistry of Acid Mine Drainage and a Method to Control Acid Formation. Ph.D. dissertation, Princeton University, Princeton, NJ, 104 pp.

Kleinmann, R.L.P., 1988. Bactericidal control of acidic drainage. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, K.B.C. Brady, M.W. Smith, and J. Schuek, eds. Pennsylvania Department of Environmental Protection, Harrisburg, PA, pp. 15.1–15.6.

Kleinmann, R.L.P., 2000. Bactericidal control of acidic drainage. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, Presented at the West Virginia Surface Mine Task Force Symposium, April 4–5, 2000, Morgantown, WV. K.B.C. Brady, M.W. Smith, and J. Schuek, eds. Pennsylvania Department of Environmental Protection, Harrisburg, PA, pp. 15.1–15.6.

Kleinmann, R.L.P., and Rastogi, V., 1994. Reducing acid mine drainage liabilites using bactericides and other control technologies. Workshop Proceedings, 13th Annual Meeting of the American Society for Surface Mining and Reclamation, Duluth, MN, 80 pp.

Kleinmann, R.L.P., Hedin, R.S., and Nairn, R.W., 1998. Treatment of mine drainage by anoxic limestone drains and constructed wetlands. In: Geogenic Acidification in Mining Lakes, W. Geller, ed. Umweltforschugszentram Leipzig-Halle GmbH, Magdeburg, Germany. Springer-Verlag, Berlin, pp. 303–320.

Kleinmann, R.L.P., and Erickson, P.M., 1981. Field evaluation of a bactericidal treatment to control acid drainage. In: Proceedings of the 1981 Symposium on Surface Mining Hydrology, Sedimentology and Reclamation, D.H. Graves, ed., University of Kentucky, Lexington, KY, December 7–11, pp. 325–329.

Knoll, A., 2003. Life on a Young Planet: The First Three Billion Years of Evolution on Earth. Princeton University Press, Princeton, NJ, 277 pp.

Knoll, A.H., Canfield, D.E., and Konhauser, K.O., 2012. Fundamentals of Geobiology. Wiley-Blackwell, Chichester, UK, 443 pp.

Konhauser, K., 2007. Introduction to Geomicrobiology. Blackwell, Malden, MA, 425 pp.

Langmuir, D., 1971. Eh–pH determination. In: Procedures in Sedimentary Petrology, R.E. Carver, ed. Wiley-Interscience, New York, pp. 597–635.

Leathen, W.W., 1976. The influence of bacteria on the formation of acid mine drainage. Abstracted in: Coal and the Environment Abstract Series: Mine Drainage Bibliography, V. Gleason and H.H. Russell, eds. Bituminous Coal Research, Monroeville, PA, 288 pp.

Leathen, W.W., Braley, S.A., and McIntyre, L.D., 1953. The role of bacteria in the formation of acid from certain sulfuric constituents associated with bituminous coal: II. Ferrous-iron oxidizing bacteria. Applied Microbiology, vol. 1, pp. 65–68.

Lindberg, R.D., and Runnels, D.D., 1984. Ground water redox reactions: an analysis of equilibrium state

applied to Eh measurements and geochemical modeling. Science, vol. 225, pp. 925–927.

Lindsey, D.A., 2007. Precambrian time—the story of the early Earth: U.S. Geological Survey Fact Sheet, pp. 2007–3004.

Luther, G.W., III, Kostka, J.E., Church, T.M., Sulzberger, B., and Stumm, W., 1992. Seasonal iron cycling in the salt-marsh sedimentary environment: the importance of ligand complexes with FeII and FeIII in the dissolution of FeIII minerals and pyrite, respectively. Marine Chemistry, vol. 40, pp. 81–103.

Madigan, M.T., Martinko, J.M., Stahl, D.A., and Clark, D.P., 2008. Brock Biology of Microorganisms, 12th ed. Benjamin Cummings, San Francisco, 1168 pp.

McGuire, M.M., Edwards, K.J., Banfield, J.F., and Hamers, R.J., 2001. Kinetics, surface chemistry, and structural evolution of microbially mediated sulfide dissolution. Geochimica et Cosmochimica Acta, vol. 65, no. 8, pp. 1243–1258.

Mielke, R.E., Pace, D.L., Porter, T., and Southam, G., 2003. A critical state in the formation of acid mine drainage: colonization of pyrite *Acidithiobacillus ferrooxidans* under pH-neutral conditions. Geobiology, vol. 1, pp. 81–90.

Mills, C., 1995a. Technical Review of the Acid Rock Drainage (ARD) and Metal Leaching Aspects of the Metallurgical Testwork, Milling Practices and Tailings Monitoring for the Huckleberry Project. Report to British Columbia Ministry of Energy, Mines and Petroleum Resources, 34 pp.

Mills, C., 1995b. An introduction to acid rock drainage. Presented at Acid Rock Drainage at the Cordilleran Roundup. Education Committee of the Mining Association of British Columbia, Vancouver, BC, Canada.

Mills, C., 1995c. The Role of Micro-organisms in Acid Rock Drainage. InfoMine Publications, Vancouver, BC, Canada, 7 pp.

Morris, J.C., and Stumm, W., 1967. Redox equilibria and measurements of potentials in the aquatic environment. In: Equilibrium Concepts in Natural Water Systems, W. Stumm, ed. Advances in Chemistry Series, vol. 67. American Chemical Society, Washington, DC, pp. 270–285.

Nadell, C.D., Xavier, J.B., and Foster, K.R., 2009. The sociobiology of biofilms. FEMS Microbiology Reviews, vol. 33, pp. 206–224.

Neuman, D.R., Brown, P., Jackson, D., and Jennings, S.R., 2009. Metals: Freshwater Fish Health and Ecology, a Literature Review. Reclamation Research Group Publication, Bozeman, MT, 73 pp.

Newman, D.K., Orphan, V.J., and Reysenbach, A.-L., 2012. Molecular biology's contributions to geobiology, In: Fundamentals of Geobiology, A.H., Knoll, D.E. Canfield, and K.O. Konhauser, eds. Wiley-Blackwell, Chichester, UK, pp. 228–249.

Noel, J., 2012. Observing Microbes—Methods to Observe Microbes. Retrieved August 13, 2012, http://microbes.org/microbiology-techniques/observing-microbes.

Nordstrom, D.K., 1977. Thermochemical redox equilibria of Zobell's solution. Geochemica et Cosmochimica Acta, vol. 41, pp. 1835–1841.

Nordstrom, D.K., 1979. Redox equilibria of iron in acid mine waters. In: Chemical Modeling in Aqueous

Systems, E.A. Jenne and J.W. Ball, eds. ACS Symposium Series, vol. 93. American Chemical Society, Washington, DC, pp. 51–79.

Nordstrom, D.K., 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In: Acid Sulfate Weathering: Pedogeochemistry and Relationship to Manipulation of Soil Minerals, L.R. Hossner, J.A. Kittrick, and D.F. Fanning, eds. Soil Science Society of America Press, Madison, WI, pp. 46–53.

Nordstrom, D.K., 2000. Aqueous redox chemistry and the behavior of iron in acid mine waters. In: Workshop on Monitoring Oxidation–Reduction Processes for Ground-water Restoration, Workshop Summary, Dallas, TX, April 25–27, R.T. Wilkin, R.D. Ludwig, and R.G. Ford, eds. Office of Research and Development, U.S. Environmental Protection Agency, Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Ada, OK, pp. 43–47.

Nordstrom, D.K., and Southam, G., 1997. Geomicrobiology: interactions between microbes and minerals. Mineral Society of America, vol. 35, pp. 261–390.

Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., and Blowes, D.W., 2000. Negative pH and extremely acidic mine waters from Iron Mountain, California. Environmental Science Technology, vol. 34, no. 2, pp. 254–258.

Ober, J.A., 2002. Materials Flow of Sulfur. Open File Report 02-298. U.S. Geological Survey, Reston, VA, 56 pp.

Pagenkopf, G.K., Russo, R.C., and Thurston, R.V., 1974. Effect of complexation on toxicity of copper to fishes. Journal of the Fisheries Research Board of Canada, vol. 31, pp. 462–465.

Plumlee, G.S., Smith, K.S., Montour, M.R., Ficklin, W.H., and Mosier, E.L., 1999. Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. In: The Environmental Geochemistry of Mineral Deposits, Part B, Case Studies and Research Topics, L.H. Filipek and G.S. Plumlee, eds. Reviews in Economic Geology, vol. 6B. Society of Economic Geologists, Littleton, CO, pp. 373–432.

Price, W.A., 2005. List of Potential Information Requirements in Metal Leaching/Acid Rock Drainage Assessment and Mitigation Work. Report 5.01E. Mining Environment Neutral Drainage Program, Canada Centre for Mineral and Energy Technology, 25 pp.

Puls, R.W., and Deutsch, W.J., 2000. Session 3 Summary: Redox Processes in Inorganic Remediation, Workshop on Monitoring Oxidation–Reduction Processes for Ground-water Restoration, Workshop Summary, Dallas, TX, April 25–27, R.T. Wilkin, R.D. Ludwig, and R.G. Ford, eds. Office of Research and Development, U.S. Environmental Protection Agency, Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Ada, OK, pp. 79–88.

Puls, R.W., and Deutsch, W.J., 2001. Redox processes in inorganic remediation. In: Monitoring Oxidation–Reduction Processes for Groundwater Restoration: A Workshop Summary. EPA/600/R-02/002. U.S. EPA, Washington, DC.

Rainey, F.A., and Oren, A., 2006. Extremophiles: Methods in Microbiology. Elsevier, London, 838 pp.

Reynolds, P.J., Sharma, P., Jenneman, G.E., and McInerney, M.J., 1989. Mechanisms of microbial movement in subsurface materials. Applied and Environmental Microbiology, vol. 55, 2280–2286.

Ritchie, A.I.M., 1994. The waste-rock environment. In: Environmental Geochemistry of Sulfide Mine-Wastes, J.L. Jambor and D.W. Blowes, eds. Mineralogical Association of Canada Shortcourse Handbook, vol. 22, pp. 133–161.

Robbins, E.I., 2000. Bacteria and archaea in acidic environments and a key to morphological identification. Hydrobiologia, vol. 433, pp. 61–89.

Robbins, E.I., Rodgers, T.M., Nordstrom, D.K., and Alpers, C.N., 2000. Ecogeochemistry of the subsurface food web at pH 0–2.5 in Iron Mt., California. Hydrobiologia, vol. 433, pp. 15–23.

Robertson, A.M., and Broughton, L.M., 1992. Reliability of acid rock drainage testing. In: Science Applications International Corporation, Predicting Acid Generation from Non-Coal Mining Wastes: Notes of July 1992 Workshop. Draft report prepared for the Environmental Monitoring Systems Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Las Vegas, NV.

Schlesinger, W.H., 1997. Biogeochemistry: An Analysis of Global Change, 2nd ed. Academic Press, San Diego, CA, 588 pp.

Schlesinger, W.H., and Bernhardt, E.A., 2013. Biogeochemistry: An Analysis of Global Change, 3rd ed. Academic Press, San Diego, CA, 688 pp.

Shaw, S., and Mills, C., 2000. Petrology and Mineralogy in ARD Prediction. InfoMine Publications, Vancouver, BC, Canada, 9 pp.

Siefert, J.L., and Fox, G.E., 1998. Phylogenetic mapping of bacterial morphology. Microbilogy, vol. 144, pp. 2803–2808.

Siegel, F.R., 2002. Environmental Geochemistry of Potentially Toxic Metals. Springer-Verlag, Berlin, 212 pp.

Sievert, S.M., Wieringa, E.B.A., Wirsen, C.O., and Taylor, C.D., 2007. Growth and mechanism of filamentous-sulfur formation by *Candidatus arcobacter sulfidicus* in opposing oxygen–sulfide gradients. Environmental Microbiology, vol. 9, pp. 271–276.

Singer, P.C., and Stumm, W., 1968. Kinetics of the oxidation of ferrous iron. In: 2nd Symposium on Coal Mine Drainage Research. Bituminous Coal Research, Inc., Monroeville, PA, pp. 12–34.

Singer, P.C., and Stumm, W., 1970. Acid mine drainage: rate-determining step. Science, vol. 167, pp. 1121–1123.

Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., and Hellier, W., 1998. Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage Acid, Technology Initiative (ADTI). From http://www.ott.wrcc.osmre.gov/library/hbmanual/hbtechavoid/hbtechavoid.pdf.

Smith, E.E., and Shumate, K.S., 1970. Sulfide to Sulfate Reaction Mechanism. Water Pollution Control Research Series 14010 FPS. U.S. Department of the Interior, Washington, DC.

Sobek, A., Schuller, W., Freeman, J.R., and Smith, R.M., 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoils. EPA-600/2-78-054. U.S. EPA, Cincinnati, OH, 203 pp.

Southam, G., and Beveridge, T.J., 1992. Enumeration of *Thiobacilli* within pH-neutral and acidic mine tailings and their role in the development of secondary mineral soil. Applied and Environmental

Microbiology, vol. 58, pp. 1904–1912.

Southam, G., and Beveridge, T.J., 1993. Examination of lipopolysaccharide (O-antigen) populations of *Thiobacillus ferrooxidans* from two mine tailings. Applied and Environmental Microbiology, vol. 59, pp. 1283–1288.

Stookey, L.L., 1970. Ferrozine: a new spectrophotometric reagent for iron. Analytical Chemistry, vol. 42, pp. 779–781.

Stumm, W., and Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria in Natural Waters, 3rd ed. Wiley-Interscience, New York, 1022 pp.

Suthersan, S., 2001. Natural and Enhanced Remediation Systems. CRC Press/Lewis Publishers, Boca Raton, FL, 419 pp.

Symonds, R.B., Rose, W.I., Bluth, G.J.S., and Gerlach, T.M., 1994. Volcanic – gas studies: methods, results, and applications. In: Volatiles in Magmas, M.R. Carroll and J.R. Holloway, eds. Mineralogical Society of America Reviews in Mineralogy, vol. 30, pp. 1–66.

Tamura, H., Goto, K., Yosuyanagi, T., and Nagayama, M., 1974. Spectrophotometric determination of iron(II) with 1,10-phenanthroline in the presence of large amounts of iron(III). Talanta, vol. 21, pp. 314–318.

Temple, K.L., and Koehler, W.A., 1954. Drainage from Bituminous Coal Mines. Engineering Experiment Station Research Bulletin 25. West Virginia University, Morgantown, WV.

Thomas, B.P., Fitzpatrick, R.W., Merry, R.H., and Hicks, W.S., 2003. Acid Sulfate Soil Technical Manual (Version 1.2): Coastal Acid Sulfate Soil Management Guidelines, Barker Inlet, SA. CISRO Land and Water, Canberra, Australia, 65 pp.

Tokody, L., 1952. Kristallographische Untersuchungen an Pyriten aus dem Karpatenbecken. Acta Geologica Academiae Scientiarum Hungancae, vol. 1, pp. 327–339.

Trevors, J.T., 2003. Origin of the first cells on Earth: a possible scenario. Geomicrobiology Journal, vol. 20, pp. 175–183.

Trevors, J.T., Elsas, J.D., van Oerbeek, L.S., and Starodub, M.-E., 1990. Transport of genetically engineered *Pseudomonas fluorescens* strain through a soil microcosm. Applied and Environmental Microbiology, vol. 56, pp. 401–408.

Tuttle, M.L.W., Breit, G.N., and Cozzarelli, I.M., 2009. Processes affecting δ34S and δ values of dissolved sulfate in alluvium along the Canadian River, central Oklahoma, USA. Chemical Geology, vol. 265, pp. 455–467.

U.S. Environmental Protection Agency, 1971. Inorganic Sulfur Oxidation by Iron-Oxidizing Bacteria. Water Pollution Control Research Series 14010 DAY. U.S. Department of the Interior, Washington, DC.

U.S. Geological Survey, 1968. Mineral Resources of the Appalachian Region. Geological Survey Professional Paper 580. U.S. Government Printing Office, Washington, DC.

U.S. Standard Atmosphere (USAA), 1976. United States Committee on Extension to the Standard Atmosphere, “U.S. Standard Atmosphere, 1976”, National Oceanic and Atmospheric Administration,

National Aeronautics and Space Administration, United States Air Force, U.S. Government Printing Office, Washington, D.C.

Waksman, S.A., 1922. Microorganisms concerned in the oxidation of sulfur in the soil: IV. A solid medium for the isolation and cultivation of *Thiobacillus thiooxidans*. Journal of Bacteriology, vol. 7, pp. 605–660.

Walton-Day, K., Macalady, D.L., Brooks, M.H., and Tate, V.T., 1990. Field methods for measurement of ground water redox chemical parameters. Ground Water Monitoring Review, Fall, pp. 81–89.

Wan, J., Wilson, J.L., and Kieft, T.L., 1994. Influence of the gas–water interface on transport of microorganisms through unsaturated porous media. Applied and Environmental Microbiology, vol. 60, pp. 509–516.

Westall, J.C., 2000. Geochemical equilibrium and the interpretation of Eh., Workshop on Monitoring Oxidation–Reduction Processes for Ground-water Restoration, Workshop Summary, Dallas, TX, April 25–27, R.T. Wilkin, R.D. Ludwig, and R.G. Ford, eds. Office of Research and Development, U.S. Environmental Protection Agency, Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Ada, OK, pp. 21–24.

White, A.F., Peterson, M.L., and Solbau, R.D., 1990. Measurement and interpretation of low levels of dissolved oxygen in ground water. Ground Water, vol. 28, pp. 584–590.

Whitfield, M., 1974. Thermodynamic limitations on the use of the platinum electrode in Eh measurements. Limnology and Oceanography, vol. 19, pp. 857–865.

Wilkin, R.T., and Ptacek, C.J., 2000. Session 4 Summary: Field Measurement of Geotechnical Redox Parameters, Workshop on Monitoring Oxidation–Reduction Processes for Ground-water Restoration, Workshop Summary, Dallas, TX, April 25–27, R.T. Wilkin, R.D. Ludwig, and R.G. Ford, eds. Office of Research and Development, U.S. Environmental Protection Agency, Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Ada, OK, pp. 89–99.

Woese, C.R., 1987. Bacterial evolution. Microbiology Reviews, June, pp. 221–271.

Woese, C.R., and Fox, G.E., 1977. Phylogenetic structure of the prokaryotic domain: the primary kingdoms (archaebacteria/eubacteria/urkaryote/16S ribosomal RNA/molecular phlogeny). Proceedings of the National Academy of Sciences USA, vol. 74, no. 11, pp. 5088–5090.

Younger, P.L., Banwart, S.A., and Hedin, R.S., 2002. Mine Water: Hydrology, Pollution, Remediation. Springer-Verlag, New York.

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TRACE ELEMENT GEOCHEMISTRY AND ACID ROCK DRAINAGE

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Acid rock drainage (ARD) and metal leaching affect the quality of our water, soil, plant, and fish habitat in terms of trace elements, in both toxic or nontoxic, and bioavailable or nonavailable forms. The degree of impact is determined by the type and concentration of the trace elements within the host medium (e.g., the mineral assemblage). Trace element geochemistry is readily determined from standard analytical tests, provided that the sample medium is collected and analyzed in a manner that includes a program of quality assurance and quality control (QA/QC). The cost of trace element analyses and geochemistry prediction is relatively inexpensive when undertaken as part of an overall ARD study.

Introduction

Metal leaching (ML) is a naturally occurring process. Conditions under which trace-element-bearing minerals formed are probably very different relative to the near-surface environment. Tectonic processes in our dynamic Earth translocate these minerals into an environment where they are metastable and so break down naturally. Secondary transport by mechanical (i.e., gravity, glaciation, anthropogenesis, etc.) and/or hydromorphic (i.e., groundwater, surface runoff, etc.) processes can enrich the receiving environment and thus, based on trace element concentration(s) and the abundance of the bearing mineral(s), manifest a potentially negative impact. Metal leaching is generally associated with acid rock drainage, but it can occur under non-ARD conditions. It is thus imperative that trace element geochemistry be a major part of any ARD study, as it is generally site-specific. Metal leaching and acid rock drainage policy and guidelines are becoming standard practice for most government environmental agencies, and the proponents should help to set the receiving environment objectives and permitting conditions. Interpretations from the results of an ARD study may be used to predict metal leaching potential; however, the time scale of metal leaching commencement, duration, and termination cannot be determined with certainty from laboratory test work. A review of geochemical software models devised for the prediction of acidic drainage does not really address the process of metal leaching (Perkins et al., 1995).

Trace element Geology

Trace elements in a geological context have been defined by Thrush et al. (1990) as “all elements except the eight abundant rock-forming elements: oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium.” The term *trace element* is generally reserved for those elements found in parts per million (ppm) concentrations in common rock-forming minerals. However, they may themselves be major constituents in certain rock formations, such as ore deposits (e.g., Cu in chalcopyrite, Zn in sphalerite, Ni in pentlandite); trace constituents in ore deposits (e.g., Cd in sphalerite); or even ultratrace constituents in non-ore minerals (e.g., Cu, Co, and Ni in pyrite). Careful selection of an analytical test is required to match the major, trace, or ultratrace character of the target constituent in test media.

Kwong (1993) examined the effect of trace elements in pyrite in his study on the weathering ability of

sulfides. His preliminary investigation concluded that “the incorporation of both interstitial impurities and mineral inclusions in pyrite will cause local strain in the crystal structure, rendering the pyrite more susceptible to alteration” and that little information is known regarding the effect of trace element content on pyrite weatherability.

The identification of problematic trace element(s) should be done at an early stage in both the exploration and feasibility stages of a project (Claridge and Downing, 1993). The costs of treating problematic trace element(s) can be very high, but if the source(s) can be identified, its selective treatment may be more cost-effective than the treatment of the much larger quantity of non-problematic material with which it is arbitrarily classified (Wilson, 1993). It is imperative that the trace element geochemistry of potential waste rock considered for blending be studied (Downing and Giroux, 1993). Blending may be a remediation for neutralization, but it may have a severe impact on trace element (metal) leaching if the waste rock is not characterized properly.

The two most common ARD-generating sulfides are pyrite and pyrrhotite. Trace elements in both these minerals can vary greatly within site and between sites (Hawley and Nichol, 1961). Trace elements of pyrite have been investigated and reported by Auger (1941), Sztrokay (1944), Bjorlykke (1947), Fleisher (1955), and Uytenbogaardt and Burke (1971). It is essential that any determinations made on pyrite or other sulfide mineral samples be done on well-defined and specified samples, such as sections of diamond drill core and/or specific locations from a mineral or mine property. Studies by Kwong and Whiteley (1993) indicate that trace heavy elements may have an impact on the weatherability of sulfides and hence the rate of ARD generation.

Site Studies

Trace element geochemistry should not be limited to acid rock generation sites but also be applied to any project that involves creating, removal, and storage of waste material such as rock, soil, and tailings. This would include industrial minerals such as diamonds and coal (Goodarzi, 1994). Mineral deposits are unique, in that each type of deposit will have a particular geochemical signature. Explorationists use trace element geochemistry to locate these deposits through analysis of rock, soil, water, and plant material (Ryall, 1977; Roberts, 1982). The tectonic environment of formation of volcanogenic massive sulfide deposits and porphyry tin and copper–molybdenum deposits can be identified from the geochemical characteristics of the associated igneous rocks (Pearce and Gale, 1975). The incorporation of trace elements into minerals occurs at the time of formation but can be altered over geological time with changes in temperature, pressure, and alteration resulting from hydrothermal fluids (Raiswell and Plant, 1980; Madeisky (1995). A plot of Mo versus depth from a drill hole that intersected disseminated nickel-bearing sulfides in dunite shows the influence of hydrothermal activity, as indicated by the elevated Mo values (Figure 4.1).

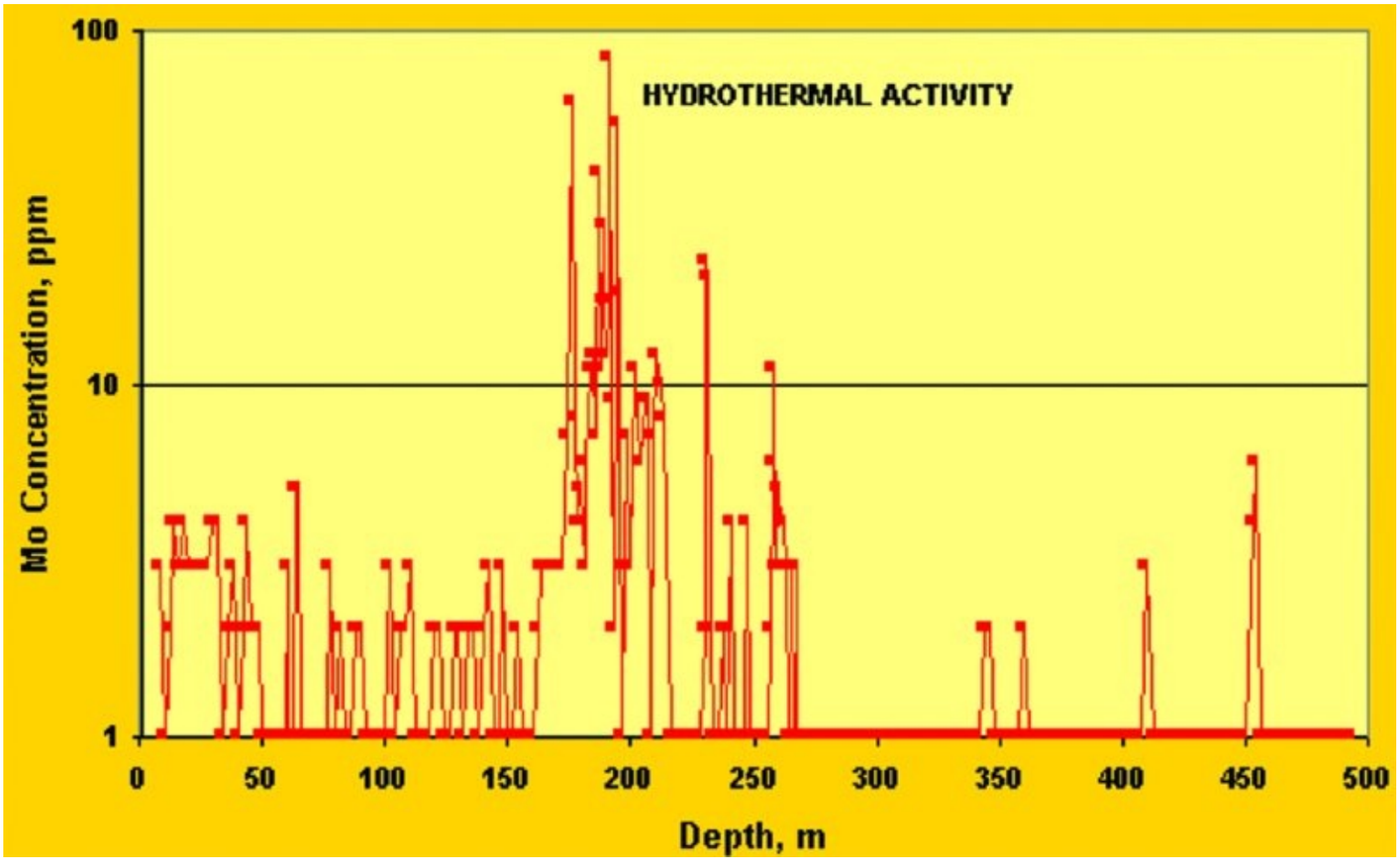

FIGURE 4.1 Variation of molybdenum concentration with depth for a diamond drill hole in nickeliferous dunite.

Metal mineralization may occur as disseminations in host rock and in veins and as massive sulfides and fracture fillings. A deposit may contain one or several of these types of metal mineralization. Each type may either have different metals and trace elements or varying concentrations of the same. This variation will certainly have an impact on waste material characterization and disposal (Downing and Giroux, 1993).

Sampling

Sampling is a major part of the program (Downing, 2011). Program requirements and location will determine the selection of the optimum sample media. Selection of an inappropriate medium and/or inadequate or inconsistent sampling procedures invariably produce data of questionable quality, leading to erroneous analysis, interpretation, and conclusions.

Analysis

Most analytical methods consist of three stages: sample preparation, decomposition, and determination. Optimization of the analysis method requires careful consideration of each component. The myriad of choices permit targeted information, ranging from total element characterization of the entire sample (i.e., bulk compositional analysis) to selective determination of a single analyte in a specific substratum or a single mineral grain. The investigator must give careful consideration to match the inherent strengths (or limitations) of the analysis method to the program requirements for accuracy (trueness of the analytical result), precision (repeatability of the analytical result within an acceptable range), and detection limit (lowest quantifiable concentration).

Preparation

Good geochemical analysis begins with a representative sample. Proper sample collection ensures adequate characterization of the geological entity. Sample preparation through processes of comminution and/or separation allows extraction of a substantially smaller subsample for analysis, yet preserves or enhances the geochemical character of the original sample either in its entirety or in part. Realistically, a mass of several tens of kilograms to several tens of thousands of metric tons may be defined by an analytical test on a 500-mg subsample. Using Gy's theorem (Gy, 1963, 1965; Ottley, 1966) and some foreknowledge of the sample material, the analyst can calculate the volume of subsample and grain size needed for a statistically valid chemical analysis. Sample reduction can entail screening to one or several size fractions, comminution by crushing and/or milling, and separation by density and/or magnetic properties. Standard procedure at most laboratories is to sieve soils and sediments to −80 mesh ASTM (American Society of Testing and Materials) (−177 μm). Rocks are crushed to −10 mesh ASTM (−2000 mm), then a riffle split subsample is pulverized to −200 mesh ASTM (−75 μm) or finer. A substantially larger subsample comprising a wide range of grain sizes may be employed if the focus of investigation is trace elements residing as coatings on mineral grains. Conversely, metals adhering to the charged surfaces of clay particles may be examined by centrifuging the clay fraction from a water suspension. Water samples generally do not require preparation other than to resuspend any settled material by agitating the sample prior to analysis.

Point-source geochemical analysis requires segregating minerals of interest. Typically, these have a higher density, so gravity separation using heavy liquids (Mills, 1986) or mechanical jigs (Burt and Mills, 1984) is used. The resulting concentrate is then “picked” by a trained mineralogist for the mineral(s) desired. The relative densities of some relevant sulfide minerals vary from 3.9 to 7.6 g/cm^3 (Table 4.1).

TABLE 4.1 Sulfide Mineral Relative Densities

	Relative Density	
Mineral	**Jones and Fleming**	**Tillé and Panou**
Arsenopyrite	5.9–6.2	
Chalcopyrite	4.1–4.3	4.1–4.3
Galena	7.4–7.6	7.5–7.6
Pyrite	5.0–5.1	4.8–5.0
Pyrrhotite	4.6	4.6–4.75
Sphalerite	3.9–4.1	3.9–4.1

Source: Jones and Fleming (1965) and Tillé and Panou (1965).

Decomposition

Sample decomposition can be total, partial, or selective, given the requirements of analysis. Fusion with fluxes such as lithium borate or sodium peroxide provides total destruction of the most resistant mineral grains, producing salts readily digested in weak acids or water. Mixtures of strong mineral acids such as hydrofluoric, perchloric, nitric, and hydrochloric acids can digest all but the most resistant minerals (e.g., zircons), thereby permitting nearly total determination of trace elements. Strong acids used singularly or in certain combinations will dissolve some minerals while leaving others intact for a partial determination of trace elements. For example, nitric acid used alone or in combination with hydrochloric

acid (aqua regia) will decompose sulfides and most metal oxides, hydroxides, and carbonates. With either total or partial decomposition, the investigator can determine the total potential load of trace metals in the environment. Liberation of the trace metals may be studied with a selective or sequential digestion scheme. A sample can be leached sequentially with distilled water, ion-exchange reagents, oxidizing or reducing agents, and weak or dilute acids and bases to progressively strip away trace metals residing in various substrates (Chao, 1984). The investigator can thus quantify bioavailability or ascertain the rate of loading of trace metals in the environment.

Determination

State-of-the-art multielement analyses are instrumental determinations measuring mass, light emission, and x-ray or gamma-radiation properties of atoms within a sample. Inductively coupled plasma emission spectrography (ICP-ES) delivering concentrations for 30 to 40 different elements is a common geochemical analysis tool. Sample solutions are aspirated into a plasma operating at 8000 K. Light emitted by excited atoms returning to the ground state is split into its spectral wavelengths by an Eschelle grating. The intensities of the various wavelengths are measured by one or more CCD chips. The linear range is five orders of magnitude, with detection limits in the ppm-to-ppb level. Inductively coupled plasma mass spectrometry (ICP-MS) capable of quantifying 60 to 70 elements is the instrument of choice for geochemical analysis. As with ICP-ES, a sample solution is aspirated into a high-temperature plasma that produces a stream of ions. The standard mass spectrometer uses a quadrupole to discriminate atoms based on their mass/charge ratio and to target a specific element for “atom counting.” Elements are sequentially counted by altering the conditions in the quadrupole. The latest generation of ICP-MS quadrupole instruments have a linear range of nine orders of magnitude, with detection limits at the low-ppb-to-ppt level. The instrument is best applied to the analysis of waters, effluents, and solutions with low concentrations of dissolved solids. High-resolution ICP-MS instruments are capable of even lower detection limits, while multidetector ICP-MS instruments can measure different isotopes of the same element simultaneously with high precision, as is required for rock genesis or geochronology work.

Instrumental neutron activation analysis is a nondestructive technique for the determination of 35 or more elements, including Au. The method is particularly well suited for the analysis of rare earths (i.e., La, Ce, Nd, etc.), incompatible elements (Hf, Nb, Ta), some trace elements (As, Co, Sb), minor elements (Ba, Rb), and major elements (Fe, Mg, Na). However, the method is inadequate for base metals (Cu, Pb, and Zn). Sample powders are encapsulated and exposed to neutron flux in the heart of a nuclear reactor. The samples are removed and allowed to cool for several days to permit decay of the more active gamma-ray emitters. Subsequently the samples are placed in a gamma-ray detector to determine element concentrations by measuring the intensities of the various gamma-ray wavelengths. The linear range is five orders of magnitude, with detection limits at ppm-to-ppb level.

A related method bombards a sample with high-energy x-rays and measures the intensity and wavelength of secondary (or fluorescent) x-rays to determine composition and concentration. Sample powders can be mixed with a binding agent and subjected to very high pressure to generate a pressed pellet, or decomposed at high temperature with a flux to produce a uniform glass wafer. The method is highly precise and effective in the determination of major and minor elements. However, typical detection limits in the tens of ppm range inhibit applications in trace-to-ultratrace element studies.

Bulk- and Single-Source Analyses

A geochemical investigation can examine either the bulk source or the single source of one or more elements within a sample. A bulk-source analysis generally doesn't discriminate the source of the

analyte(s) in question, even when focusing on a particular size fraction, density fraction, or sample substrate. On the contrary, a single-source analysis may examine the partial or total composition of a specific mineral type or even an individual mineral crystal.

Bulk-source analyses may focus on a single element using an analyte-specific method (e.g., gold fire assay) or a total compositional analysis using a group of analytical methods to gain maximum information about a sample. Regional-scale surveys using bulk-source analysis of sediment, soil, and rocks may be employed to define the metallogeny and economic potential of large areas. Property-scale surveys using bulk source analyses of soils, rocks, and drill core may define the presence and economic viability of an ore deposit. Whole-rock analysis [by x-ray fluorescence (XRF) or by ICP-ES/ICP-MS] is a type of bulk-source analysis commonly employed on rock samples to determine their exact composition. In combination with petrographic and mineralogical analysis, this can define the rock type and possibly its genesis and postgenesis history. One tool gaining popularity is the mineral liberation analyzer (Gu, 2003), which consists of an automated scanning electron microscope and energy-dispersive x-ray spectrometry to map out the composition, mineralogy, and textural relationships. A sample analysis may cost hundreds to thousands of dollars, due to the high cost of the instrument and the time required to scan, analyze, map, and interpret the hundreds to hundreds of thousands of mineral grains present within a sample. Use in exploration will increase in proportion to decreasing analytical costs in the future.

Bulk-source analyses also employ partial digestions or leaches wherein optimizing the contrast between anomalous and background samples is paramount. Many proprietary leaches, such as MMI (mobile metal ion) and Enzyme Leach, attack only the most labile form of elements present within soil samples. Research (Hamilton, 2005) has occasionally shown the coincidence between surface anomalies detectable by these weak leaches and oxidizable deposits buried at considerable depth.

Single-source analysis is limited to specific minerals (or mineral grains) and is generally carried out employing petrographical and mineralogical examination using transmitted and reflected light microscopy, and by various x-ray diffraction techniques. Although electron probe microanalysis, scanning electron microscopy, and other more specialized techniques are employed, their use is generally confined to sulfide minerals, where compositional abnormalities affect ARD test work interpretation. Such techniques are particularly useful in determination of the chemical composition of sulfide oxidation products, such as rims, inclusions, and amorphous (noncrystalline) species.

Case Study: Former Britannia Mine

The Britannia mine was operated in British Columbia from 1902 to 1963 by the Britannia Mining and Smelting Company Ltd., and from 1963 to 1974 by the Anaconda Mining Company. Mining activity ceased in 1974 because of the exhaustion of ore that could be extracted economically. Because of an environmental concern for ARD, water quality monitoring continued into the late 1990s. Most of the underground workings of the mine are currently relatively inaccessible, and representative rock sampling is not possible. However, Table 4.2 shows some major, minor, and trace elemental analyses for three tailings samples and one ore sample from the former Britannia mine during production. These analyses are reported in DBARD3, the British Columbia database for acid rock drainage (Lawrence and Harries, 1996), but their source and history are not known.

TABLE 4.2 Major, Minor, and Trace Elemental Analyses for Four Rock Samples from the Former Britannia Copper Mine.

	Sample Name and Number			
	Tailings,	**Ore,**	**Tailings,**	**Tailings,**
Element	**880355-071**	**C6**	**880355-072**	**880355-076**
Al (%)	2.68	4.44	7.17	7.44
As (ppm)	3450	80	—	—
Ag (ppm)	—	—	0.2	
B (ppm)				
Ba (ppm)	70	2130	90	90
Ca (%)	4.15	0.4	3.74	3.19
Cd (ppm)	1	15	2	2.5
Co (ppm)	36.9	34	16	11
Cr (ppm)	37.7	8	54	56
Cu (ppm)	3450	—	196	75
Fe (%)	9.06	—	5.78	5.16
Hg (ppm)				
K (%)	—	—	0.34	0.36
Li (ppm)				
Mg (%)	2.33	2.9	1.62	1.69
Mn (ppm)	1260	96	1235	1060
Mo (ppm)	—	8	3	1
Na (%)	0.052	0.2	3.99	4.19
Ni (ppm)	19	30	11	8
Pb (ppm)	80	400	48	14
Sb (ppm)				
Se (ppm)				
Si (%)	0.341	1.6		
Sn (ppm)	—	20		
Sr (ppm)	155	40	162	147
V (ppm)	267	30	248	247
Zn (ppm)	272	2610	78	72

Source: Lawrence and Harries (1996).

The elements present in the ore and tailing samples may be divided into four groups, depending on their concentration:

1. Major rock-forming mineral elements: Al, Ca, Fe, K, Mg, Mn, Na, and Si.

2. Major ore-mineral elements: As (one sample, probably tennantite), Cu, Fe, and Zn (chalcopyrite, pyrite, sphalerite).
3. Trace elements: Ag (argentite), Ba (barite), Cd, Co, Cr, Mo, Ni. Pb (galena), Sn, (celestite), and V.
4. At or below detection limit or not determined: B, Hg, Li, Sb, and Se.

Table 4.3 shows acid--base accounting (ABA) properties for the three tailing samples. With NPR values of 0.26, 0.22, and 0.19, all three of the tailing samples are considered to be potentially acid generating.

TABLE 4.3 Acid--Base Accounting Properties for Three Rock Samples from the Former Britannia Copper Mine

	Sample Name and Number		
ABA Property	**Tailings, 880355-071**	**Tailings, 880355-072**	**Tailings, 880355-076**
Sulfide, S (%)	1.3	1.26	2.25
AP (kg/mt $CaCO_3$)	40.6	39.3	70.3
NP, Sobek (kg/mt $CaCO_3$) NPR (NP/AP)	10.8	10.3	13.7
	0.26	0.22	0.19

Source: Lawrence and Harries (1996).

Figure 4.2 shows total metal concentrations and pH for the 2200-ft-level-portal discharge (ARD) at the Britannia mine for a 17-week period during 1995. The elements present in the 2200-ft-level effluent (ARD) may be divided into four groups, depending on their concentration:

1. Major elements, >10 mg/L: Al, Ca, Cu, Fe, Mg, Si,Zn
2. Minor elements, <10 to >0.1 mg/L: Bi, Cd, Mn, Sr
3. Trace elements, <0.1 mg/L: As, B, Ba, Co, Ni, Pb, Sn,Ti
4. At or below detection limit: Ag, Be, Cr, Mo, Sb, Se, Te, Tl, V, Zr

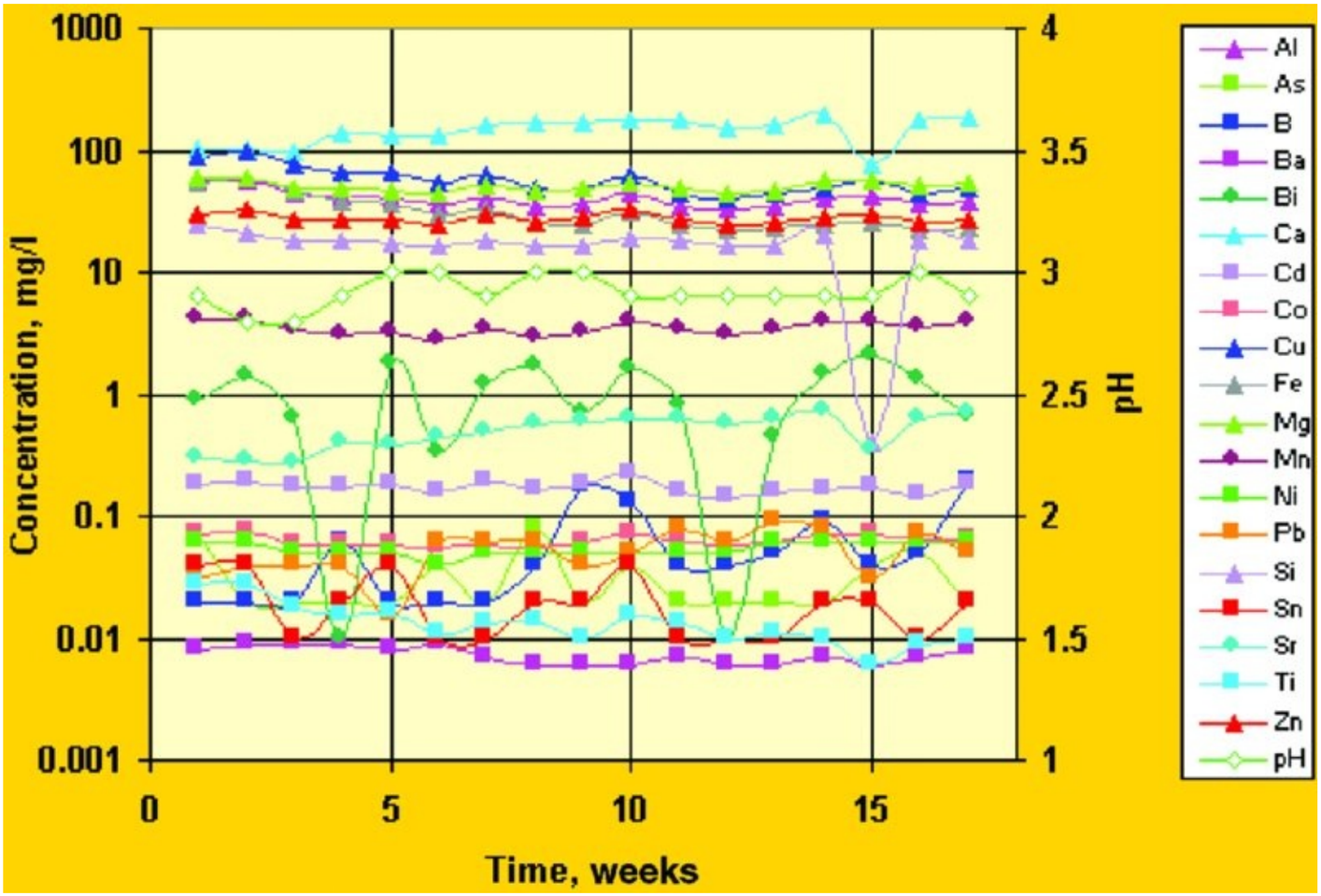

FIGURE 4.2 Major, minor, and trace element monitoring data, 2200-ft-level adit effluent (ARD), Britannia mine, BC, 1995. (Data courtesy of Gordon Ford, BC Ministry of Environment.)

Although the actual tailings analyzed and reported in Tables 4.2 and 4.3 are not claimed to be representative of the rock source of the ARD discharging from the 2200-ft-level (Figure 4.2), they were produced from the Britannia mine. The trace elements Ba, Cd, Co, Ni, Pb, and Sr in the rock (tailings) samples all appear as trace or minor elements in the ARD. The major rock-forming mineral elements Al, Ca, Fe, Mg, and Si are major elements in the ARD, indicating the probable dissolution of calcite, dolomite, and aluminosilicates (K and Na analyses were not conducted on the ARD), and Mn is present as a minor element. The major ore mineral elements Cu, Fe, and Zn are all major elements in the ARD. Arsenic appears as a trace element in the ARD (although it was reported to be below detection limits for more than 50% of the samples), but was reported for only one of the samples.

In general terms, the discussion above demonstrates that trace metal concentrations in ARD can be predicted qualitatively, and possibly semiquantitatively, from the chemical mineralogical and analyses of host rock and ore. A more detailed analysis, including that of individual sulfide mineral grains, would indicate trace element--mineral associations such as Ni and Co with pyrite and/or chalcopyrite, and Cd with sphalerite.

Data Analysis

The methods for determination of natural and elevated-to-toxic concentrations of both dissolved and nondissolved components in various media lend themselves to both statistical and elemental plotting techniques. Runnells et al. (1998) have shown that probability plots can be used to determine natural

background concentrations of dissolved components in water at mining, milling, and smelting sites. It is up to the ARD proponent and consultants to analyze and present the data in a meaningful form for regulatory agencies and the public to understand and comprehend.

Summary

Trace element content and distribution will vary from lithology to lithology and site to site; however, the commonality is sample collection, sample preparation, analytical technique, data analysis, and reporting.

References and Suggested Reading

Auger, P.E., 1941. Zoning and district variations of the minor elements in pyrite of canadian gold deposits. Economic Geology, vol. 36, pp. 401–423.

Bjorlykke, H., 1947. Flaat nickel mine. Norges. Geolgiske Undersoekelse, 168 pp.

Burt, R.O., and Mills, C., 1984. Gravity Concentration Technology. Advances in Mineral Processing Series, vol. 5, Elsevier, Amsterdam, 617 pp.

Chao, T.T., 1984. Use of partial dissolution techniques in geochemical exploration. Journal of Geochemical Exploration, vol. 20, pp. 101--135.

Claridge, P.G., and Downing, B.W., 1993. Environmental geology and geochemistry at the Windy Craggy massive sulphide deposit, north-western British Columbia. CIM Bulletin, vol. 86, no. 966, pp. 50–57.

Downing, B., 2011. ARD Sampling and Preparation. Technology Paper. InfoMine Publications, Vancouver, BC, Canada, 15 pp. httt://technology.informine.com/environmine/ard/sampling/intro.html#sample. Accessed July 21, 2013.

Downing, B.W., and Giroux, G., 1993. Estimation of a waste rock ARD block model for the Windy Craggy massive sulphide deposit, northwestern British Columbia. Exploration and Mining Geology, vol. 2, no. 3, pp. 203–215.

Downing, B.W., and Madeisky, H.E., 1999. Lithogeochemical methods for ARD prediction. Exploration and Mining Geology, vol. 6, no. 4.

Fleischer, M., 1955. Minor elements in some sulfide minerals. Economic Geology 50th Anniversary Volume, pp. 970–1024.

Goodarzi, F., 1994. Inorganic constituents of coal and their impact on coal quality. CIM Bulletin, vol. 7, no. 983, pp. 47–56.

Gu, Y., 2003. Automated scanning electron microscope based mineral liberation analysis: an introduction to JKMRC/FEI mineral liberation analyser. Journal of Minerals and Materials Characterization and Engineering, vol. 2, no. 1, pp. 33–41.

Gy, P.M., 1963. The sampling of broken ores: a review of principle and practice. In: Proceedings of the 5th International Mineral Processing Congress. Institute of Mining and Metallurgy, London, pp. 16–27.

Gy, P.M., 1965. Sampling of ores and metallurgical products during continuous transport. Transactions of

the Institution of Mining and Metallurgy, vol. 7, pp. 165--195.

Hamilton, S., 2005. Electrochemical transport, reduced chimneys and “forest rings” over oxidizable geological features: understanding the physics. AAG Distinguished Lecturer Series. Association of Applied Geochemists, Nepean, ON, Canada.

Hawley, J.E., and Nichol, I., 1961. Trace elements in pyrite, pyrrhotite and chalcopyrite of different ores. Economic Geology, vol. 56, no. 3, pp. 467–487.

Jones, M.P., and Fleming, M.G., 1965. Identification of Mineral Grains. Elsevier, London, pp. 32--35.

Kwong, Y.T.J., 1993. Prediction and Prevention of Acid Rock Drainage from a Geological and Mineralogical Perspective. MEND Report 1.32.1, NHRI Contribution CS-92054. MEND, Ottawa, ON, Canada.

Kwong, Y.T.J., and Whiteley, W.G., 1993. Heavy metal attenuation in northern drainage systems. In: International Northern Research Basins Symposium/Workshop, Canada, p. 18.

Lawrence, R.W., and Harries, L.M., 1996. DBARD for Paradox: Developments in DBARD the Database for Acid Rock Drainage. MEND Report 1.12.1b. MEND Secretariat, Ottawa, ON, Canada.

Madeisky, H.E., 1995. Quantitative analyses of hydrothermal alteration: applications in lithogeochemical exploration. Presented at the Pacific Northwest Mining and Metals Conference. Society for Mining, Metallurgy and Exploration and the Association of Exploration Geochemists, Vancouver, BC, Canada. Short course notes, 234 pp.

Mills, C., 1986. Specific gravity fractionation and testing with heavy liquids. In: SME Mineral Processing Handbook. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, Sect. 30, pp. 44–52.

Ottley, D.J., 1966. Gy's sampling slide rule. Mining and Minerals Engineering, October, pp. 390–395.

Pearce, J.A., and Gale, G.H., 1975. Identification of ore-deposition environment from trace-element geochemistry of associated igneous host rocks. Earth Planetary Scientific Letters, vol. 31, pp. 14–24.

Perkins, E.H., Nesbitt, H.W., Gunter, W.D., St.-Arnaud, L.C., and Mycroft, J.R., 1995. Critical Review of Geochemical Processes and Geochemical Models Adaptable for Prediction of Acidic Drainage from Waste Rock. MEND Report 1.42.1. MEND, Ottawa, ON, Canada, 120 pp.

Rasiwell, R., and Plant, J., 1980. The incorporation of trace elements into pyrite during diagenesis of black shales, Yorkshire, England, Economic Geology, vol. 75 no. 5, pp. 684--699.

Roberts, F.I., 1982. Trace element chemistry of pyrite: a useful guide to the occurrence of sulfide base metal mineralization. Journal of Geochemical Exploration, vol. 17, pp. 49–62.

Runnels, D.O., Dupon, D.P., Jones R.L., and Cline, O.J., 1998. Determination of natural background concentrations of dissolved componetns in water at mining, milling and smelting sites. Mining Engineering, February, pp. 65--71.

Ryall, W.R., 1977. Anomalous trace elements in pyrite in the vicinity of mineralized zones at Woodlawn, N.S.W., Australia. Journal of Geochemical Exploration, vol. 8, pp. 73–83.

Sztrokay, K. von, 1944. Erzmikroskopische Beobachtungen an Erzen von Recsk (Matra Banya) in Ungarn. Neues Jarhbuch für Mineralogie, A, vol. 79, pp. 104–128.

Thrush, P.W., et al., 1968. A Dictionary of Mining, Mineral and Related Terms. Special Publication. U.S. Bureau of Mines, Department of the Interior, Washington, DC.

Tillé, R., and Panou, G., 1965. Methodes de determination des mineraux, 2nd ed. Presses Universitaires de Bruxelles, Brussels. Belgium, 113 pp.

Uytenbogaardt, W., and Burke, E.A.J., 1971. Tables for Microscopic Identification of Ore Minerals, 2nd ed., Elsevier, New York, 206 pp.

Wilson, G.C., 1993. Mineralogy of Sulphide Ores from the H-W Deposit, Vancouver Island, B.C., with Emphasis on the Mineralogical Residence of Gold, Silver and Arsenic. Annual Technical Report, VMS Project. Mineral Deposits Research Unit, University of British Columbia, Vancouver, BC, Canada.

5
THE MICROBIOLOGY OF ACID DRAINAGE

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The environmental sulfur cycle involves many physical, chemical, and biological agents. A simplified schematic diagram of the cycle is shown in Figure 5.1, which has been prepared to show the major phases of sulfur cycling in relation to mineral deposits. As such, the figure indicates the relationships between sulfur, S; hydrogen sulfide, H_2S; sulfur dioxide, SO_2; and the sulfate ion, SO_4^-. In mineral form, sulfur may be present as sulfides (e.g., pyrite, FeS_2; chalcopyrite, FeS·CuS; pyrrhotite, FeS) and/or sulfates (e.g., gypsum, $CaSO_4 \cdot 2H_2O$; barite, $BaSO_4$). Sulfur in minerals may move through the cycle as a result of the oxidation of sulfides to sulfate and/or the dissolution of sulfates. For example, oxidation of pyrite to sulfuric acid may be followed immediately, in situ, by acid neutralization by calcium carbonate (calcite) to form calcium sulfate (gypsum). The reaction of hydrogen sulfide with dissolved metal ions may precipitate metallic sulfides which are chemically indistinguishable from naturally occurring sulfide minerals.

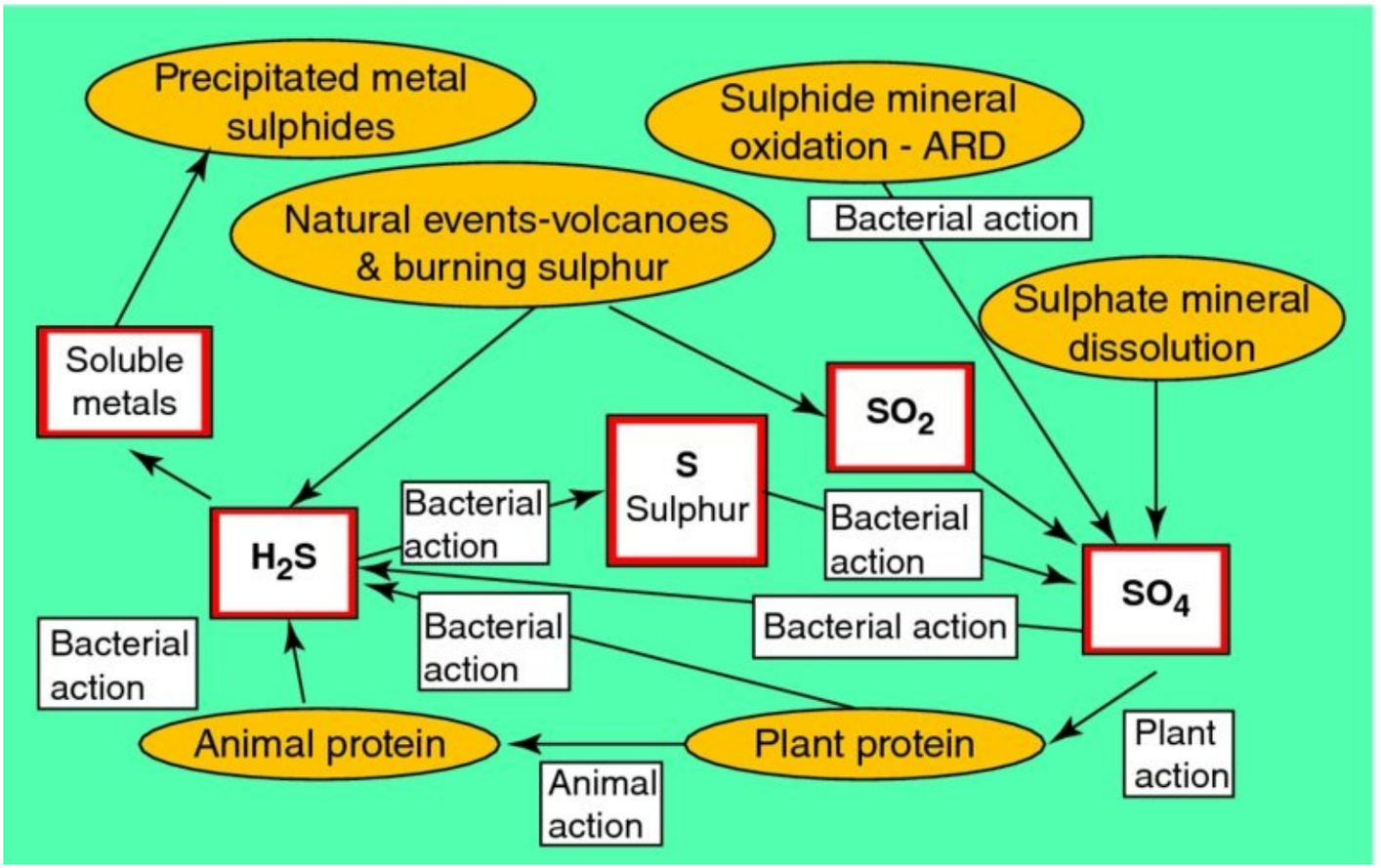

FIGURE 5.1 Simplified sulfur cycle for mineral deposits.

At some mines, sulfur is added to the cycle as sulfur dioxide in processes such as the Inco/SO_2 process for cyanide destruction in the treatment of tailings. This added sulfur is oxidized to sulfate ion (Ingles and Scott, 1987), most of which remains free but some of which combines with lime, CaO, in the tailings to

form gypsum. For information on the sulfur cycle with respect to water quality monitoring, see the Canadian guidelines (Canadian Council of Environment Ministers, 1987).

Role of Microorganisms in the Sulfur Cycle

Microorganisms (most frequently, bacteria) are often integrally involved in the chemical alteration of minerals. Minerals, or intermediate products of their decomposition, may be directly or indirectly necessary for microorganisms' metabolism. The dissolution of sulfide minerals under acidic conditions, the precipitation of minerals under anaerobic conditions, the adsorption of metals by bacteria or algae, and the formation and destruction of organometallic complexes are all examples of indirect microorganism participation. Where minerals are available as soluble trace elements, serve as specific oxidizing substrates, or are electron donors or acceptors in oxidation–reduction (redox) reactions, they may be directly involved in cell metabolic activity.

There are three categories of oxidation–reduction reactions for minerals with microorganisms:

1. Oxidation by autotrophic (cell carbon from carbon dioxide) or mixotrophic (cell carbon from carbon dioxide or organic matter) organisms. Energy derived from the oxidation reaction is utilized in cell synthesis.
2. Electron acceptance by minerals (reduction) for heterotrophic (cell carbon from organic matter) and mixotrophic bacteria. Chemical energy is used to create new cell material from an organic substrate.
3. Electron donation by minerals (oxidation) for bacterial or algal photosynthesis (reaction is fueled by photon energy).

Natural Oxidation in the Sulfur Cycle

In the 1970s and earlier, the oxidation of sulfur or sulfides for energy production was believed to be restricted to the bacterial genera *Thiobacillus*, *Thiomicrospira*, and *Sulpholobus*. These bacteria all produce sulfuric acid (i.e., hydrogen ions, H^+, sulfate and ions, SO_4^-) as a metabolic product. Extensive reviews of these bacteria and their behavior have been published (Trudinger, 1971; Brierley, 1978). Evangelou and others in the 1990s noted that these bacteria are known to accelerate the generation of acid rock drainage (ARD) from pyritic and pyrrhotitic rocks under suitable conditions. Evangelou and Zhang (1995) report that sulfide oxidation catalyzed by bacteria may have reaction rates six orders of magnitude (i.e., 1 million times) greater than the same reactions in the absence of bacteria. Figure 5.2 illustrates the shape and appearance of *Thiobacillus ferrooxidans*: The bacteria develop flagella only if they are required for mobility in accessing energy sources.

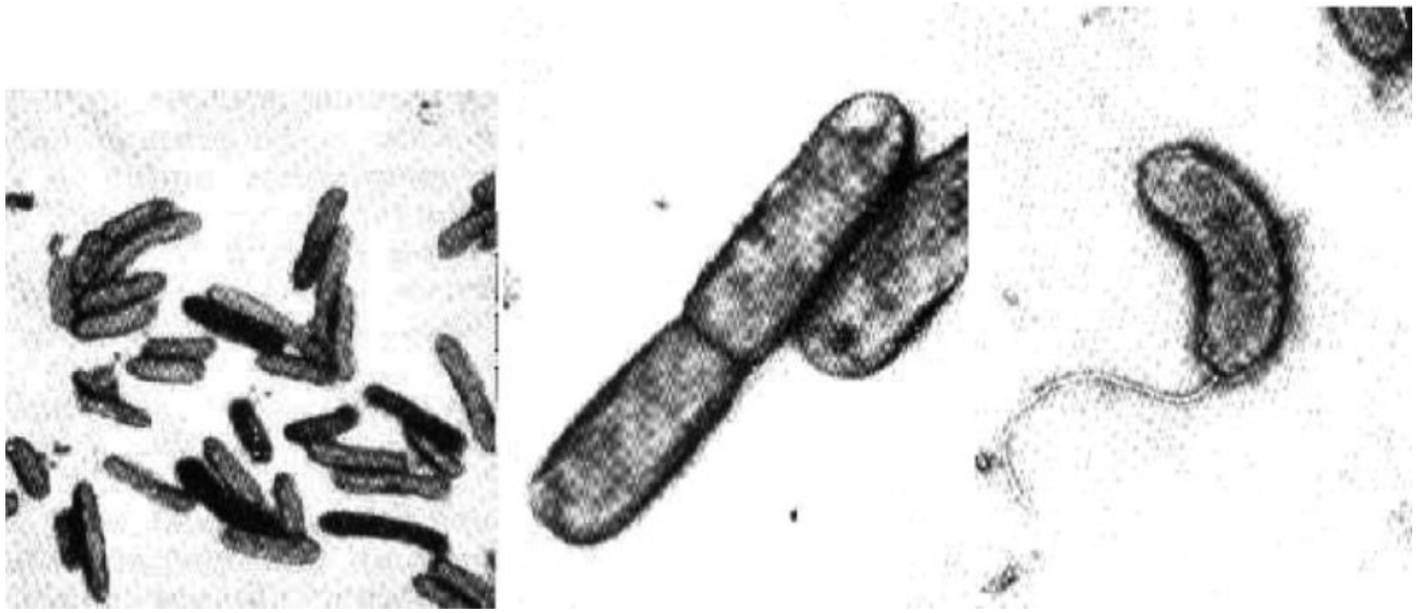

FIGURE 5.2 Thiobacilli (a,b) from bacterial generator (no flagella) and (c) grown on ferrous iron (flagella). Magnification about ×5000 (a), ×20,000 (b), ×15,000 (c). (From LeRoux et al., 1974.)

The literature prior to about 2000 reports acid drainage to be a product formed by the atmospheric (i.e., by water, oxygen, and carbon dioxide) oxidation of the relatively common iron–sulfur minerals pyrite and pyrrhotite in the presence of (catalyzed by) bacteria (*T. ferrooxidans*) and as any other products generated as a consequence of these oxidation reactions. After the early 2000s, these bacteria were renamed *Acidothiobacillus ferrooxidans*. In addition, the original tests that were used to identify the iron-oxidizing bacteria were based on isolation of the bacteria in a culture medium. Based on genetic testing, it is now known that numerous other iron-oxidizing species were growing in the environment in addition to the originally identified *T. ferrooxidans*.

An important reaction involving *T. ferrooxidans* and other iron-oxidizing bacteria is the oxidation of ferrous to ferric iron (Fe^{2+} to Fe^{3+}):

$$4Fe^{3+} + O_2 + 4H^+ = Fe^{3+} + 2H_2O$$

Ferric iron is a powerful oxidizing agent. Even at a Fe^{3+}/Fe^{2+} ratio of 1 : 1,000,000, a redox potential greater than +0.4 V is generated, which is sufficient for the attack of most base metal sulfides (Dutrizac and MacDonald, 1974). The general equation for the ferric ion reaction with base metal sulfides is

$$MS + nFe^{3+} = M^{n+} + S + nFe^{2+}$$

Consequently, in generating Fe^{3+}, *T. ferrooxidans* is indirectly responsible for the dissolution of base metal sulfide minerals and the mobilization of metallic cations such as Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}. Base metal sulfides react only very slowly with sulfuric acid in the absence of ferric iron (Roman and Benner, 1973).

The importance of redox potential in determining metal solubility and transport can be seen clearly for copper in the Eh–pH diagram for the $Cu–H_2O–O_2–S–CO_2$ system (Figure 5.3). The effects of bacteria on the rate of dissolution of copper from chalcopyrite are highly pronounced, as demonstrated by Malouf and Prater (1961) (Figure 5.4). In general, for substantial metal mobilization from base metal sulfides, the following conditions must be met (Roman and Benner, 1973):

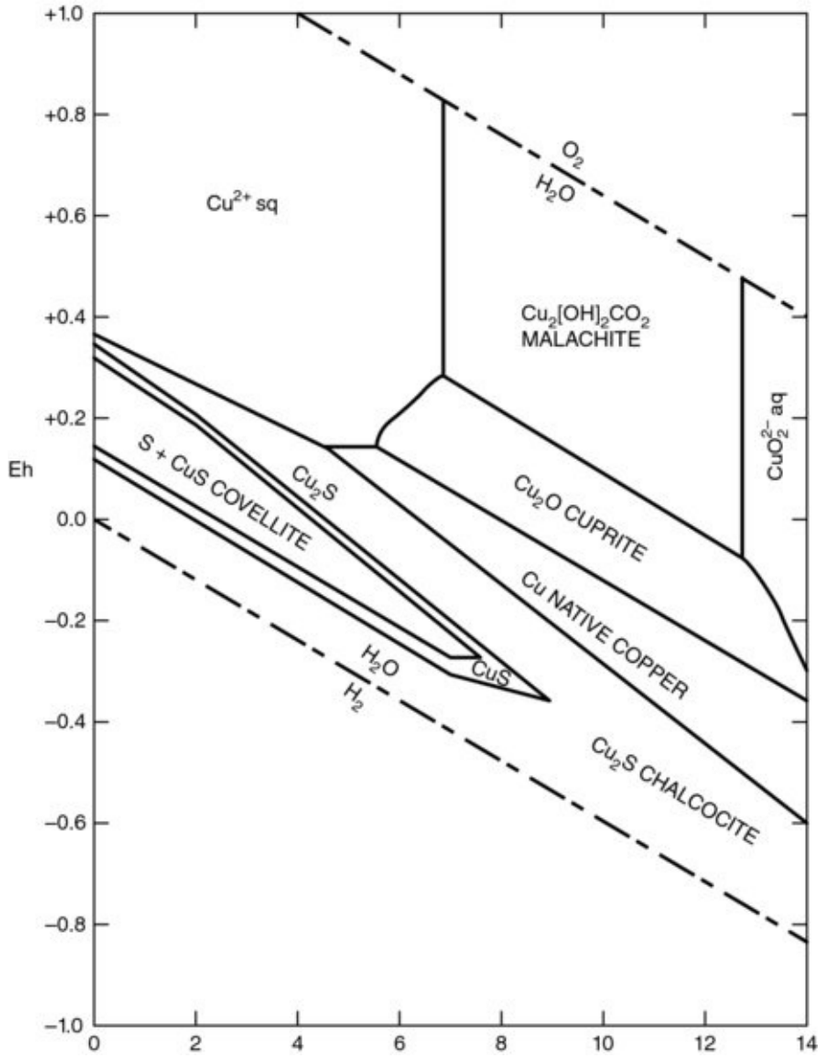

FIGURE 5.3 Eh–ph diagram for a Cu–H_2O–O_2–S–CO_2 system. (From Garrels and Christ, 1965.)

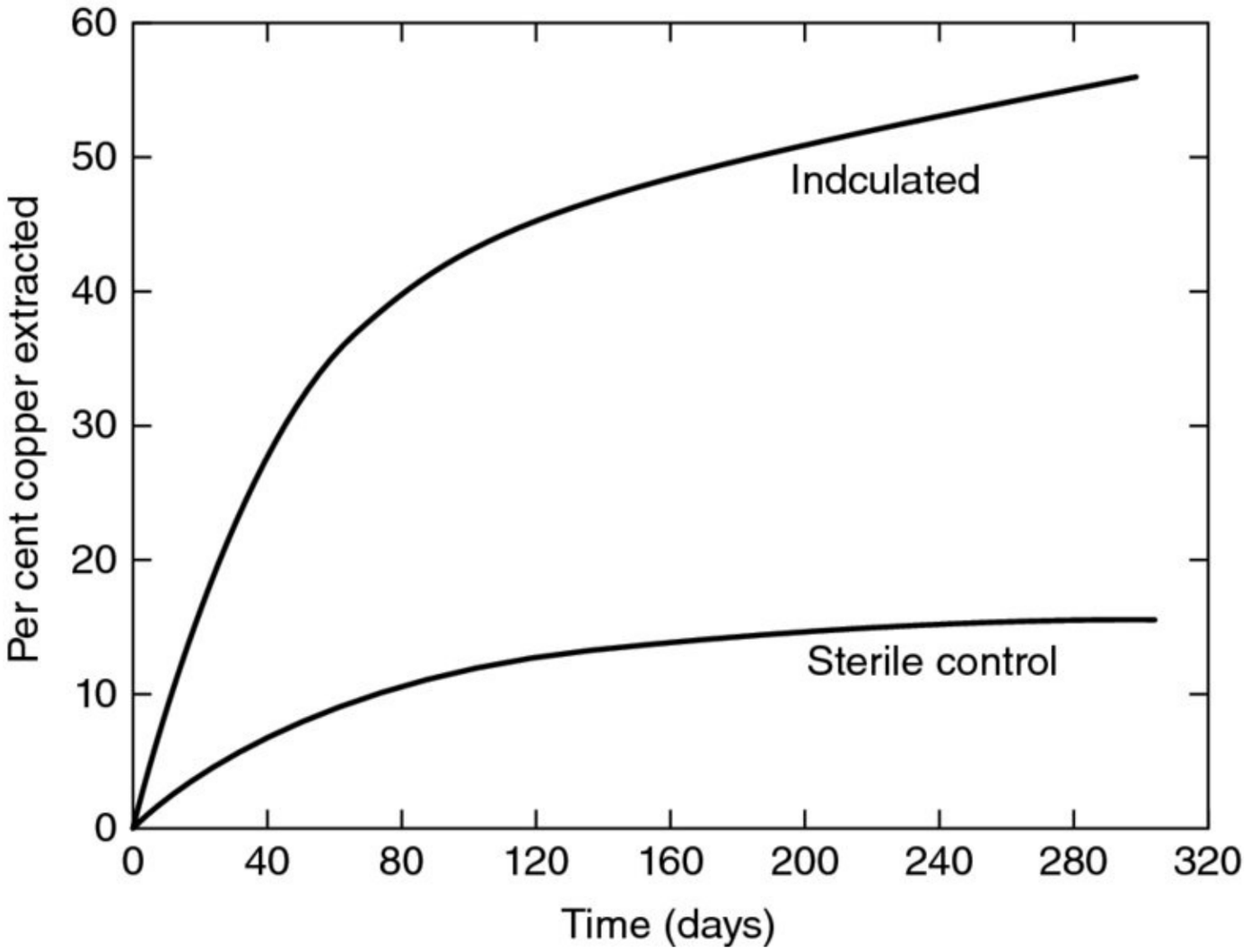

FIGURE 5.4 Effects of bacteria on the rate of disolution of copper from chalcopyrite. (From Malouf and Prater, 1961.)

- Ferric iron for sulfide oxidation
- *T. ferrooxidans* and oxygen for ferrous-to-ferric oxidation
- pH compatible with *T. ferrooxidans* habitat requirements, typically pH 1.5 to 3.5

The typical habitat pH of *T. ferrooxidans*, 1.5 to 3.5, is not one that develops spontaneously. It is currently believed (Béchard, 1996) that these conditions are produced by a consortium of bacteria acting in succession. Such a succession may include *T. thioparus* at neutral pH, giving way to dominance by *Metallogenium* bacteria under mildly acidic conditions (pH 3.5 to 4.5) (Walsh and Mitchell, 1972), and finally, *T. ferrooxidans* dominance at low pH. The metabolic activity of *T. ferrooxidans* is temperature dependent, peaking at about 30 to 35°C and falling with both increasing and decreasing temperature (Roman and Benner, 1973). Leduc and Ferroni (1994) have demonstrated that *T. ferrooxidans* strains are site-specific.

From the discussion above it is clear that consideration of bacterial behavior is most important in understanding the process of ARD generation. This is particularly so when “kinetic” tests are used to predict the rate of generation of ARD in the field. Only if the bacterial conditions of test work are identical to those in the field can rates of ARD generation and/or metal solubilization be taken from laboratory kinetic test work and used to predict field behavior with any degree of confidence.

Natural Reduction in the Sulfur Cycle

The direct reduction of sulfate ions to hydrogen sulfide is effected in nature by specialized, strictly anaerobic bacteria of the genera *Desulphovibrio* and *Desulphotomaculum*. These sulfate-reducing bacteria (SRB) are heterotrophic (cell carbon from organic compounds) organisms that utilize sulfate, thiosulfate, $S_2O_3^-$, sulfite, SO_3^-, or other reducible sulfur-containing ions as terminal electron acceptors in their respiratory metabolism. In the process these sulfur-containing ions are reduced to hydrogen sulfide.

The bacteria require an organic substrate, usually a short-chain acid such as lactic or pyruvic acid. In nature, such substrates are generated by the fermentation activities of other anaerobic bacteria on more complex organic substrates. Thus, in natural systems, the specific requirement by the SRB for a short-chain acid is met by the availability of a complex organic source and a mixed bacterial system. Lactate is used by the SRB during anaerobic respiration to produce acetate according to the reaction (Cork and Cusanovich, 1979)

$$2CH_3CHOHCOO^- + SO_4^- = 2CH_3COO^- + 2HCO_3^- + H_2S$$

This is the major natural process for the conversion (destruction) of sulfate ion. However, the process may be adapted to a controlled engineering process by the use of anaerobic reaction vessels and carbon monoxide, CO, and hydrogen, H_2, or partially oxidized propane or natural gas as the energy source for the bacteria (Warkentin and Rowley, 1994). This process of sulfate ion to hydrogen sulfide conversion is the first stage of a pilot plant that operated in 1996 at the former Britannia mine site in British Columbia, where the second stage utilized the hydrogen sulfide generated to precipitate Cu^{2+}, Zn^{2+}, and Cd^{2+} ions from ARD as metallic sulfides (Warkentin and Rowley, 1994). Further information, including details of the performance of this pilot plant, may be found at the NTBC Research Corporation website.

Steffen, Robertson and Kirsten (BC), Inc. (1991) proposed use of the underground mine at Faro, Yukon Territory as a giant underground SRB reactor to convert ARD sulfate ion to hydrogen sulfide, and to precipitate zinc contained in the ARD as zinc sulfide. The system proposed would use the mixed bacterial system present in liquid cow manure as an SRB source, and sugar as a bacterial carbohydrate (energy) source.

SRB activity in natural wetlands is capable of metal sulfide precipitation from ARD as a result of sulfate-to-hydrogen sulfide reduction, and this concept may be extended to constructed wetlands. André Sobolewski treats this subject in considerable detail at his website, Wetlands for Treatment of Mine Drainage. Reviews of this subject have also been published by the Mine Environment Neutral Drainage (MEND) program (MEND, 1990, 1993).

Other Microorganism Reactions in the Sulfur Cycle

Sulfate ion is taken up from soil by plants, which incorporate it into protein, and plant protein is consumed by animals, converting plant protein to animal protein. The death of plants and animals allows bacterial decomposition of protein in remains to produce hydrogen sulfide and other products in processes involving many fungi, actinomycetes, and bacteria such as the heterotroph *Proteus vulgaris*. Some bacteria can function in the transition zone between aerobic and anaerobic environments. Hydrogen sulfide may be oxidized to sulfur by such bacteria, which deposit elemental sulfur in their cells while using oxygen as the terminal electron acceptor. Hydrogen sulfide may also be oxidized to sulfate

photosynthetically by the Chromatiaceae and Chlorobiaceae bacterial families.

Acknowledgment

The basic material and concepts for this chapter were developed in part by the late Chris Mills, a mining engineer specializing in metallurgical engineering and surface chemistry. He was heavily involved as an engineer in the mining industry throughout the world for over 30 years, and as a teacher and researcher he contributed many technical papers and classes on mining and acid rock drainage. Sadly, he died unexpectedly on February 10, 1999.

References and Suggested Reading

Ahonen, L., and Tuovinen, O.H., 1994. Solid phase alteration and iron transformation in column bioleaching of a complex sulphide ore. In: Environmental Geochemistry of Sulphide Oxidation. C.N. Alpers and D.W. Blowes, eds. ACS Symposium Series 550. American Chemical Society, Washington, DC, pp. 79–89.

Béchard, G. (Natural Resources Canada), 1996. Personal communication to C. Mills.

Bhatti, T.M., Bigham, J.M., Vuorinen, A., and Tuovinen, O.H., 1994. Alteration of mica and feldspar associated with the microbiological oxidation of pyrrhotite and pyrite. In: Environmental Geochemistry of Sulphide Oxidation. C.N. Alpers and D.W. Blowes, eds. ACS Symposium Series 550. American Chemical Society, Washington, DC, pp. 90–105.

Brierley, C.L., 1978. Bacterial leaching. CRC Critical Reviews in Microbiology, vol. 6, no. 3, pp. 207–262.

Brierley, C.L., 1982. Microbiological mining. Scientific American, vol. 247, no. 2, pp. 44–53.

Bruynesteyn, A., and Hackl, R.P., 1984. Evaluation of acid production potential of mining waste materials. Minerals and the Environment, vol. 4, no. 1, pp. 5–8.

Canadian Council of Resource and Environment Ministers, 1987. Canadian Water Quality Guidelines CCREM, Ottawa, ON, Canada.

Colmer, A.R., Temple, K.L., and Hinkle, M.E., 1950. An iron-oxidizing bacterium from the drainage of some bituminous coal mines. Journal of Bacteriology, vol. 59, pp. 317–332.

Cork, D.J., and Cusanovich, M.A., 1979. Continuous disposal of sulphate by bacterial mutualism. Developments in Industrial Microbiology, vol. 20, pp. 591–602.

Dutrizac, J.E., and MacDonald, R.J.C., 1974. Ferric ion as a leaching medium. Minerals Science and Engineering, vol. 6, no. 2, pp. 59–100.

Ehrlich, H.L., 1990. Geomicrobiology, 2nd ed. Marcel Dekker, New York, 646 pp.

Ehrlich, H.L., and Brierley, C.L., eds., 1990. Microbial Mineral Recovery. McGraw-Hill, New York, 454 pp.

Evangelou, V.P., and Zhang, Y.L., 1995. A review: pyrite oxidation mechanisms and acid mine drainage prevention. Critical Reviews in Environmental Science and Technology, vol. 25, no. 2, pp. 141–199.

Garrels, R.M., and Christ, C.L., 1965. Solutions, Minerals and Equilibria. Harper & Row, New York, pp. 216–222.

Greenberg, A.E., Clesceri, L.S., Eaton, A.D., and Franson, M.A.H., eds., 1992. Iron and sulphur bacteria. In: Standard Methods for the Examination of Water and Wastewater, 18th ed. American Public Health Association, Washington, DC, Section 9240.

Ingles, J., and Scott, J.S., 1987. State-of-the-Art of Processes for the Treatment of Gold Mill Effluents. Unpublished report. Environmental Protection Service, Ottawa, ON, Canada. pp. 6–32 to 6–46.

Kelly, D.P., 1988. Evolution of the understanding of the microbiology and biochemistry of the mineral leaching habitat. In: Biohydrometallurgy: Proceedings of the International Symposium, Warwick, 1987; Kew, Surrey, UK, P.R. Norris and D.P. Kelly, eds. Antony Rowe Ltd., Science and Technology Letters, pp. 3–14.

Lawrence, R.W., and Sadeghnobari, A., 1986. Referenced in: Lawrence, R.W., Poling, G.W., and Marchant, P.B., 1989. Investigation of Predictive Techniques for Acid Mine Drainage. Report on DSS Contract 23440-7-9178/01-SQ, MEND Report 1.16.1(a). Energy Mines and Resources, Canada, MEND, Ottawa, ON, Canada.

Leathen, W.W., Braley, S.A., and McIntyre, L.D., 1953. The role of bacteria in the formation of acid from certain sulphuric constituents associated with bituminous coal: II. Ferrous-iron oxidizing bacteria. Applied Microbiology, vol. 1, pp. 65–68.

Leduc, L.G., and Ferroni, G.D., 1994. The Need for *Thiobacillus ferrooxidans* Strain Selection in Applications of Bioleaching. In: Proceedings of Biominet, 10th Annual General Meeting. Minister of Supply and Services Canada, Ottawa, ON, Canada, pp. 25–42.

LeRoux, N.W., North, A.A., and Wilson, J.C., 1974. Bacterial oxidation of pyrite. In: Proceedings of the 10th International Mining Congress 1973. Institute of Mining and Metallurgy, London, pp. 1051–1066.

Lizama, H.M., and Suzuki, I., 1987. Bacterial leaching of a sulphide ore by *Thiobacillus ferrooxidans* and *thiooxidans*: I. Shake flask studies. Biotechnology and Bioengineering, vol. 32, pp. 110–116.

Malouf, E.E., and Prater, J.D., 1961. Role of bacteria in the alteration of sulphide. Journal of Metals, vol. 13, pp. 353–356.

Mine Environment Neutral Drainage Program, 1990. Assessment of Existing Natural Wetlands Affected by Low pH, Metal Contaminated Seepages (Acid Mine Drainage). MEND Report 3.12.1a. Natural Resources Canada, Ottawa, ON, Canada.

Mine Environment Neutral Drainage Program, 1993. Treatment of Acidic Seepages Using Wetland Ecology and Microbiology: Overall Program Assessment. MEND Report 3.11.1. Natural Resources Canada, Ottawa, ON, Canada.

Rastogi, V., et al., 1984. Laboratory methods for determining the effects of bactericide on acid mine drainage. In: Proceedings of the 1984 Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation, Lexington, KY.

Rastogi, V., et al., 1985. The effects of particle size distribution on the rate of mine acid formation and its mitigation by bacterial inhibitors. In: Proceedings of the American Society of Mining and Reclamation,

Denver, CO.

Roman, R.J., and Benner, B.R., 1973. The dissolution of copper concentrates. Minerals Science and Engineering, vol. 5, no. 1, pp. 3–24.

Silverman, M.P., and Lundgren, D.G., 1959. Studies on the chemolithotrophic iron bacterium *Ferrobacillus ferrooxidans*: 1. An improved medium and a harvesting procedure for securing high cell yields. Journal of Bacteriology, vol. 77, pp. 642–647.

Steffen, Robertson and Kirsten B.C., Inc., 1991. Sulphate Reduction as a Water Treatment Alternative at the Faro Mine. Report for Curragh Resources, Inc., 64 pp.

Temple, K.L., and Colmer, A.R., 1951. The autotrophic oxidation of iron by a new bacterium, *Thiobacillus ferrooxidans*. Journal of Bacteriology, vol. 62, pp. 605–611.

Trudinger, P.A., 1971. Microbes, metals and minerals. Minerals Science and Engineering, vol. 3, no. 4, pp. 13–25.

Walsh, F., and Mitchell, R., 1972. A pH dependent succession of iron bacteria. Environmental Science and Technology, vol. 6, no. 9, pp. 809–812.

Warkentin, D.D., and Rowley, M.V., 1994. Britannia Minesite A.R.D. Biosulphide Demonstration Project —Interim Report—Laboratory Testing. NTBC Research Corp., Richmond, BC, Canada, 21 pp.

6
Natural Acid Rock Generation, Drainage, and Metal Leaching: Impact on Exploration, Mining, and Reclamation

BRUCE W. DOWNING

Many environmental practitioners, governments, and the public in general fail to recognize the impact and significance of natural acid rock generation and drainage (ARGD) and related metal leaching (ML) on the "earth media" (i.e., rock, soil, water) and the interactions between them over time. ARGD and ML have occurred throughout geological time and will continue as natural processes, albeit potentially influenced by anthropogenic activities. These processes need not be construed as detrimental to our perception of the natural environment but as processes to which the environment adjusts over geological time.

Introduction

Acid rock generation and drainage and metal-leaching processes have been ongoing throughout geological time and will continue into the future. ARGD and ML are natural *perpetual reaction processes*. Added to these are human-made (anthropogenic) effects that exacerbate the processes by breaking up acid-generating material so as to increase the rate of ML in many areas, be it mining, construction, or other development projects that require removal and disposal of acid-generating material. Significant amounts of heavy metals may be solubilized by these processes. In this chapter are documented some of the historical ARGD events that have affected the evolution of mineral deposits prior to their discovery and/or the mining of them. It also documents the use of background values in establishing guidelines for reclamation.

Acid Rock Drainage

The term *acid rock drainage* is a misnomer, as it implies drainage from an acid-generating source; however, the acid-generating source may not be connected with drainage. Acid rock drainage is often referred to as acid mine drainage, which occurs only in association with mining activity. The term *acid mine drainage*, as commonly used in the published literature, implies that acid generation occurs only at mine sites and does not recognize that the process is a naturally occurring one that has been taking place for millions of years. Therefore, the term *acid rock generation and drainage* should be considered more appropriate for the description of natural events, even though acid rock drainage is the accepted generic descriptive term in Canada.

ARGD is produced by atmospheric oxidation of the relatively common iron–sulfur minerals pyrite and marcasite (FeS_2), pyrrhotite (FeS), and other products generated as a consequence of these oxidation reactions in the presence of the naturally occurring sulfur-consuming bacteria *Thiobacillus ferrooxidans* (Mills, 1995). More recently, a variety of other sulfide-oxidizing microbes have been identified. Significant amounts of heavy metals may be solubilized by this process as the pH is reduced through the generation of sulfuric acid. When the process occurs naturally, geoscientists measuring the levels of metals or sulfate in surface water or groundwater and/or soils usually infer the presence of sulfide mineralogy. Surface-to-subsurface alteration of rocks, usually oxidation, resulting from ARGD, either in

situ or at some distance from the source of generation (dispersion halo), is referred to as *gossan*, and examples are shown in Figures 6.1 to 6.4.

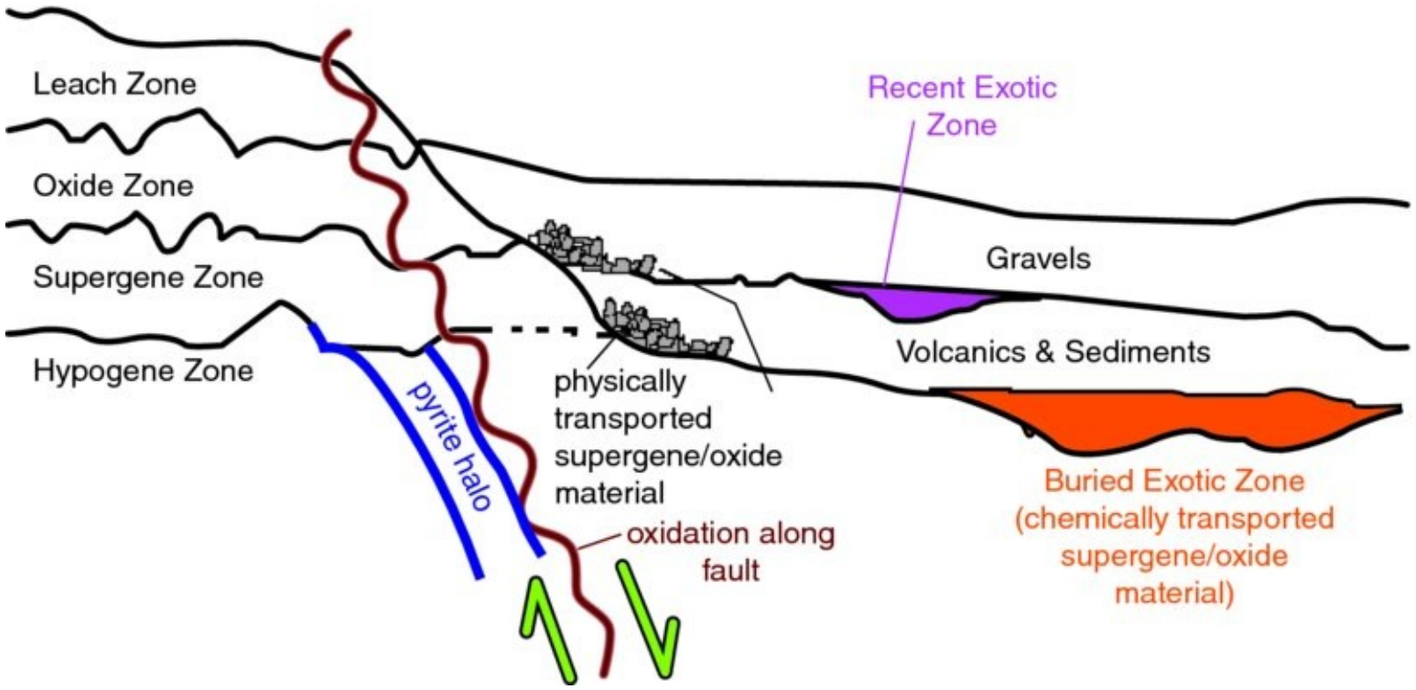

FIGURE 6.1 Formation of mineral zones derived from hypogene material.

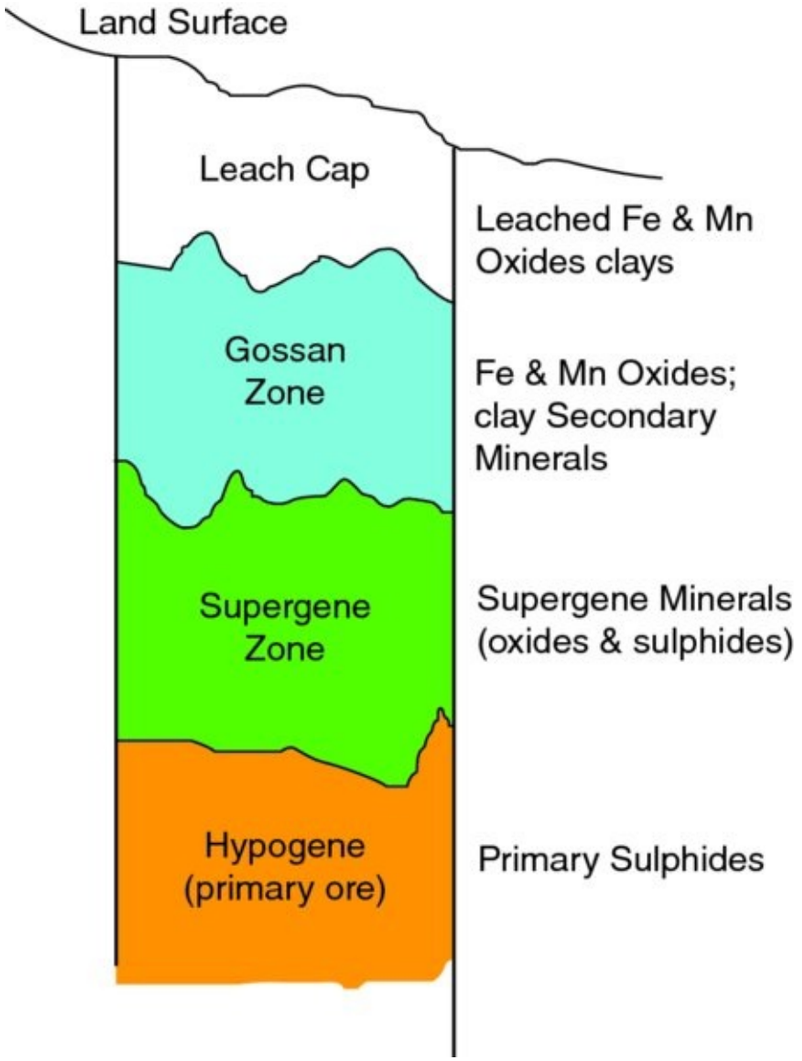

FIGURE 6.2 Mature gossan profile.

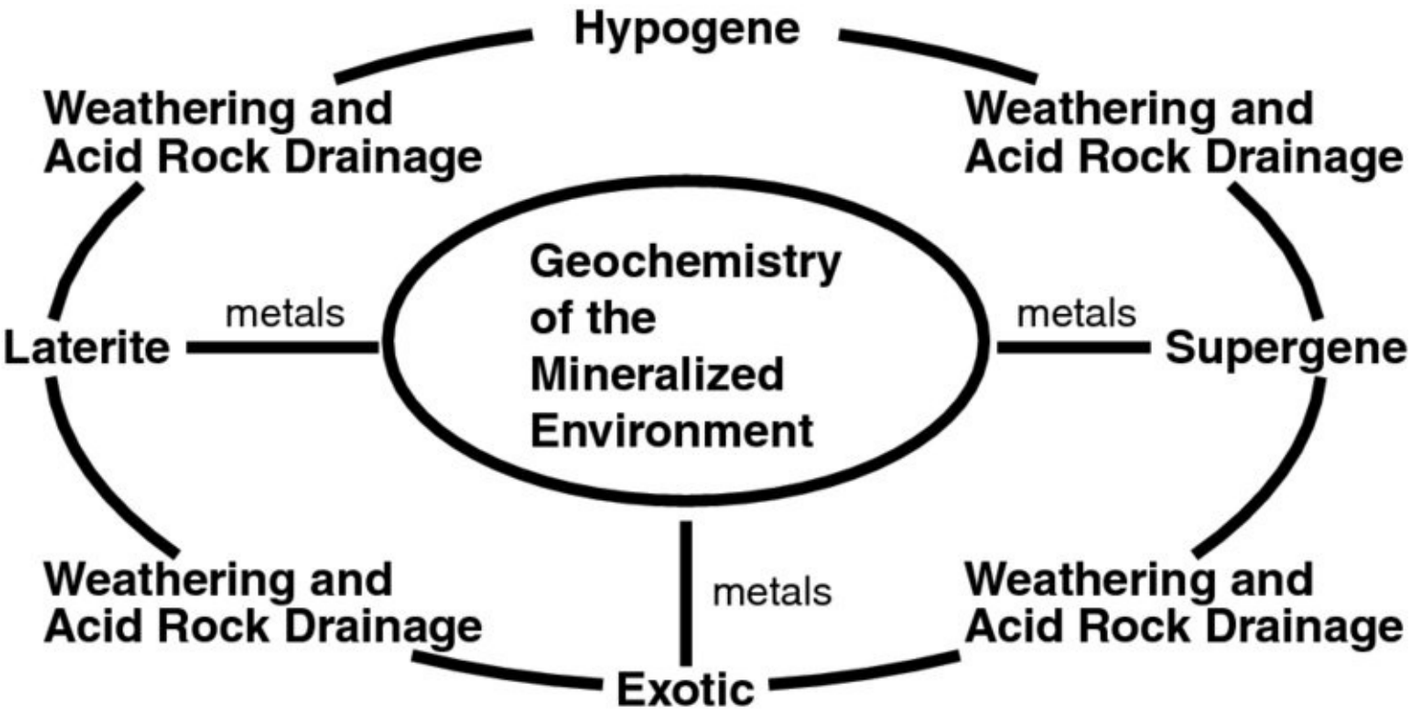

FIGURE 6.3 Weathering and acid rock generation and drainage cycle of mineralization and their impact on the geochemistry of the environment.

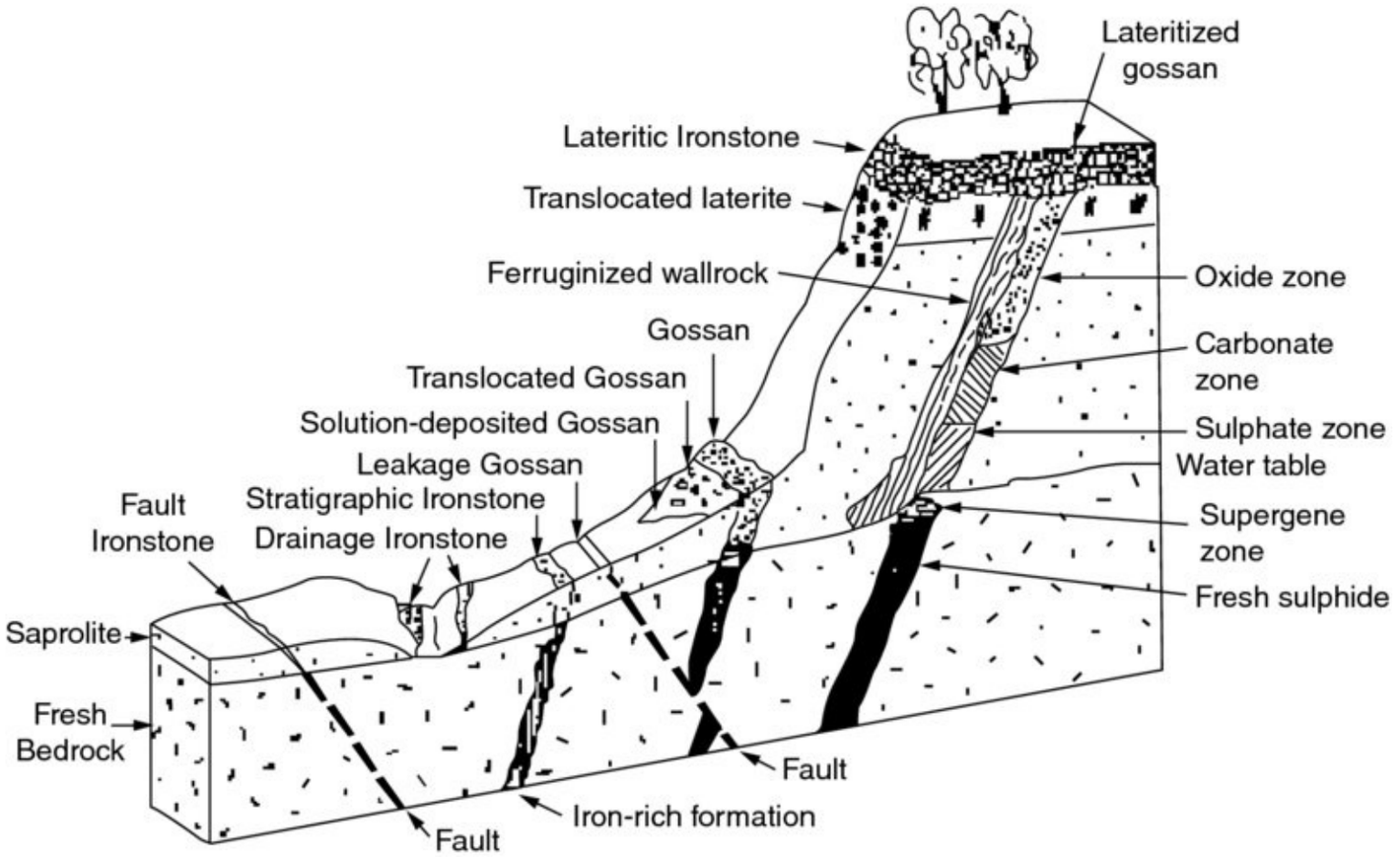

FIGURE 6.4 Mechanisms of sulfide oxidation and gossan formation. (From Taylor and Thornber, 1995.)

ARGD encompasses a pH range from 1 to 6, depending on the severity of the environment (e.g., buffering mineralogy, sulfide mineralogy, water flow, residency). Since micas and clays behave like acids in water, the pH may not always be due to ARGD, although ARGD may be the initial cause of the breakdown of the

original minerals, leading to the development of micas and clays. ARGD affects surface and subsurface water and may result in elevated levels of various chemical compounds and metals, due to metal leaching. Groundwater ARGD and ML effects on terrestrial animals and plants, and to a lesser degree aquatic organisms, resulting from groundwater combining with surface water are detectable at a distance from the actual source, depending on the groundwater flow regime or path and the type of substrate the water passes through and/or with which it comes into contact.

In a mineralized area, oxide–supergene development is an ARGD process, which is described in detail later. Exotic deposits may form in conjunction with the supergene oxidation process, whereby mineral-rich acidic solutions migrate laterally from the supergene zone by vertical and horizontal percolation within the vadose zone. Mineral-rich solutions may be transported through paleodrainage systems for up to several kilometers from the source, resulting in continuous mineral precipitation (Munchmeyer, 1996). These natural acid rock drainage processes result in in situ changes (i.e., coloration) that may lead a prospector or geoscientist to investigate the sources of mineralization. Laterization as a major process of ore deposit formation with respect to the Amazon region is discussed by da Costa (1997). Laterization does not necessarily imply acid rock drainage processes, but where sulfides are present, ARGD will occur.

Oxide–supergene processes, which can take place over several million years, may result in supergene enrichment that forms significant tonnages and an enriched grade that it may be economical to mine. These types of deposits form a dominant copper resource in South America. Some examples of supergene-enriched copper porphyry deposits and massive sulfide deposits that have a supergene manto with indicated grade, tonnage, and approximate age are shown in Table 6.1. Unfortunately, many public databases do not classify oxide–supergene mineralization as a separate ore category when reporting tonnage and grade; therefore, this table is by no means complete. Another type of oxide deposit is that of secondary iron deposits derived from the oxidation of iron sulfides.

Table 6.1 Examples of Oxide and Supergene Deposits

					Grades					
					Copper	Gold	Iron	Zinc	Age (years)	
Deposit Category	**Data Source**	**Location**	**Type**	**Tonnage**	**(%)**	**(g/mt)**	**(%)**	**(%)**	**Formed**	**Geological Period**
Porphyry										
Kemess South	Annual report	BC, Canada	Leach cap	21 mt	0.06	0.73	—	—	130 Ma	Cretaceous
	Annual report	BC, Canada	Supergene	25 mt	0.34	0.77	—	—	131 Ma	Cretaceous
	Annual report	BC, Canada	Oxide	—	—	—	—	—	10,000	Pleistocene
Afton	MinFile	BC, Canada	Supergene	30 mt	—	—	—	—	—	Upper Eocene
Bell	MinFile	BC, Canada	Supergene	—	—	—	—	—	—	Pre-Pleistocene
Berg	MinFile	BC,	Supergene	—	—	—	—	—	10,000	Pleistocene

		Canada	and oxide							
Big Onion	MinFile	BC, Canada	Supergene	32 mt	0.34	—	—	—	10,000	Pleistocene
Getty North	MinFile	BC, Canada	Supergene	36 mt	0.47	—	—	—	10,000	Pleistocene
Getty South	MinFile	BC, Canada	Supergene	72.1 mt	0.31	—	—	—	10,000	Pleistocene
Gibralter	MinFile	BC, Canada	Supergene	—	—	—	—	—	10,000	Pleistocene
Krain	MinFile	BC, Canada	Supergene	4.9 mt	0.64	—	—	—	10,000	Pleistocene
Maggie	MinFile	BC, Canada	Oxide	—	—	—	—	—	10,000	Pleistocene
Casino	MinFile	Yukon	Oxide	28 mt	0.11	—	—	—	10,000	Pleistocene
	MinFile	Yukon	Supergene	86 mt	0.43	—	—	—	10,000	Pleistocene
Taurus	MinFile	Alaska	Supergene	—	—	—	—	—	10,000	Pleistocene
Chuquicamata	Sillitoe (1996)	Chile	Supergene	2,200 mt	1.4	—	—	—	15–19 Ma	Mid-Miocene
La Escondida	Sillitoe (1996)	Chile	Supergene	1,700 mt	1.6	—	—	—	16–19 Ma	Mid-Miocene
Ujina	Camus et al. (1996)	Chile	Supergene	158 mt	1.66	—	—	—	—	Late Eocene–early Oligiocene
Quebrada Blanca	Camus et al. (1996)	Chile	Supergene	89 mt	1.3	—	—	—	—	Late Eocene–early Oligiocene
Zaldivar	Camus et al. (1996)	Chile	Supergene	246 mt	1.02	—	—	—	—	—
Huinquintipa	Camus et al. (1996)	Chile	Exotic	7 mt	1.9	—	—	—	—	Late Eocene–early Oligiocene
El Tesoro	Camus et al. (1996)	Chile	Exotic	310 mt	0.76	—	—	—	—	Late Eocene–early Oligiocene
Damiana	Camus et al. (1996)	Chile	Exotic	300 mt	0.5	—	—	—	—	Late Eocene–early

										Oligiocene
Massive sulfide										
Windy Craggy	Annual report	BC, Canada	Supergene	30 mt	1.4	0.36	—	—	—	Triassic
Zinc										
Skorpion	Borg et al. (2003)	Namibia	Supergene	24.6 mt	—	—	—	10.6	545 Ma	—
Iron										
Battlement Creek	MinFile	BC, Canada	Oxide	12,000	—	—	49	—	10,000	Pleistocene
Chilicotin	MinFile	BC, Canada	Oxide	114,000	—	—	49	—	10,000	Pleistocene
Denain Creek	MinFile	BC, Canada	Oxide	20,000	—	—	47	—	10,000	Pleistocene
FEO Creek	MinFile	BC, Canada	Oxide	15,900	—	—	48	—	10,000	Pleistocene
Forrest	MinFile	BC, Canada	Oxide	74,000	—	—	45	—	10,000	Pleistocene
Limonite	MinFile	BC, Canada	Oxide	348,000	—	—	50	—	10,000	Pleistocene
Limonite Creek	MinFile	BC, Canada	Oxide	3,175,000	—	—	44	—	10,000	Pleistocene
Rae Creek	MinFile	BC, Canada	Oxide	98,700	—	—	49	—	10,000	Pleistocene

Source: Camus et al. (1996); Brimhall et al. (1985).

Gossan Formation

Mechanisms of sulfide oxidation and gossan formation are well described by Taylor and Thornber (1995). These authors demonstrate that an understanding of the processes and conditions that can change a particular sulfide assemblage into a gossan, or subsequently into an ironstone, is based on assemblage origin, with mineralogy and geochemistry being described in terms of climate, topographic relief, type of mineralization, nature of wall rocks, nature of groundwaters, weathering history, and intrinsic properties. Gossan development over the same deposit may vary in texture and composition as a function of parental material (Thornber et al., 1981).

Generally, iron-sulfide-bearing deposits have a rust or yellow surface expression (i.e., an oxidized cap), due to oxidized sulfide minerals, and result from three processes: sulfide oxidation and dissolution, precipitation of secondary minerals, and pervasive rock leaching. Gossans have been a target of mineral prospectors throughout human history, and there are numerous examples of gossan discovery leading

eventually to major economic mining projects. Explorationists use these natural ARGD products as an aid to mineral exploration. Weathered sulfide-bearing boulders (which are indicative of ARGD), are also used by prospectors to follow up and locate the source of mineralization.

Many metal-tolerant plants occur naturally in areas of acid rock drainage. Although high metal toxicity can leave areas of "kill zones," some plants do survive on the fringes and with time gradually can overgrow these zones. Many paleogossans are covered with vegetation. A biogeochemistry exploration technique that analyses plant and tree material can be used as a guide to buried metal deposits (Brooks, 1972). It is interesting to note on maps that some topographical features have ARGD-related descriptive names, such as Gossan Island, Red Mountain, Red Creek, or Sulfide Creek or Bitter Creek, Iron Creek, and Alum Creek, as in the case of the Summitville mine area in Colorado. Many waterways, such as creeks and lakes, may be devoid of life due to natural ARGD effects, which can dramatically affect their pH and metal(s) content and toxicity to life forms. When acidic streams merge with nonacidic streams, iron oxides are often precipitated, causing the stream sediments and gravels (boulders) to become stained (Figures 6.5 and 6.6). These figures show low- and high-pH streams affecting the immediate environment.

FIGURE 6.5 Iron oxide precipitation at a confluence of creeks, Berg copper deposit, northern British Columbia. (Copyright by K. Fletcher and D. Baylis, by permission.)

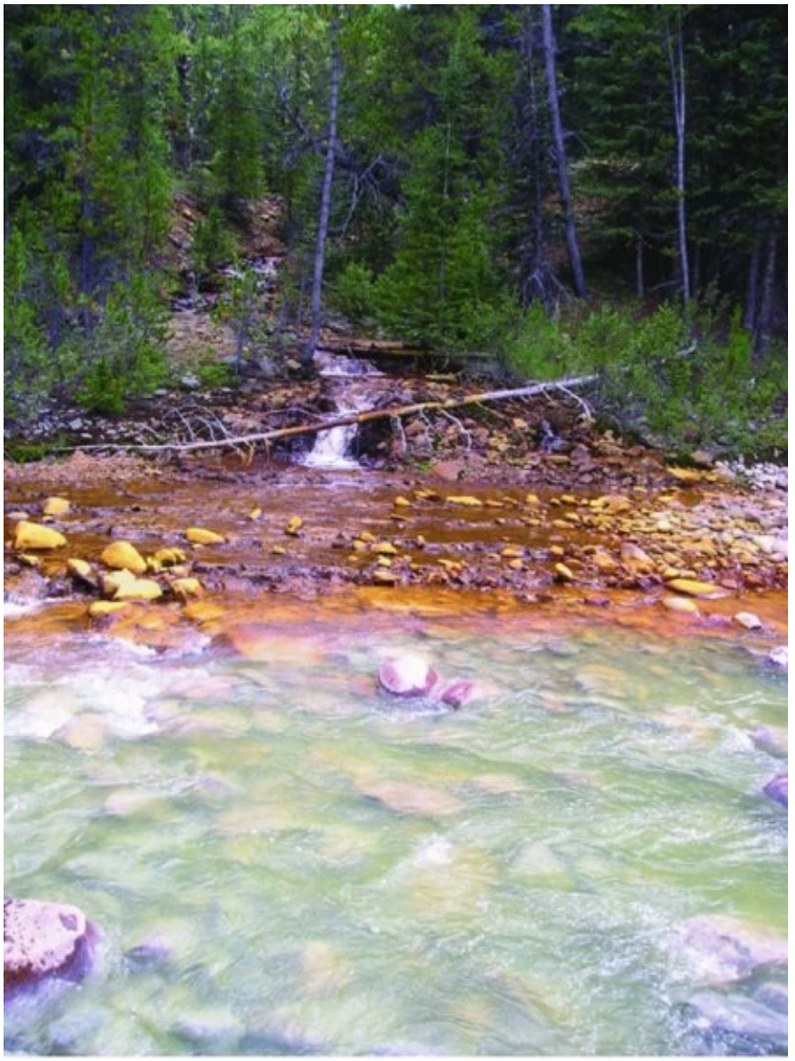

FIGURE 6.6 Confluence of south fork of Lake Creek (foreground) with a pH between 5 and 6 and an unnamed stream with a pH of 2.3 in the Sawatch Range, Colorado. Ferricrete terraces are being precipitated actively by the iron-rich stream. (Courtesy of D. Coulter.)

Gossan and related alteration can be recognized and mapped using satellite imaging data. This method has been used extensively and successfully by explorationists in locating prospective mineral sites generated from natural acid rock generation and related alteration of rocks, particularly in nonvegetated (arid) terrain. The method, known as the *Crosta technique*, is a multivariate statistical technique that uses multispectral image channels. These detect anomalous concentrations of hydroxyl, hydroxyl plus iron oxide, and iron oxide, and display the pixels (or area) in red–green–blue space color. The technique and a case study are reviewed in a paper by Laughlin (1991). Other methods incorporating various analytical techniques coupled with airborne visible and infrared data have been used to map hydrothermal and supergene alteration associated with naturally occurring acid drainage (Coulter, 2006). Gossan discoloration is sometimes a desirable feature, such as for use as decorative stone on buildings (Figures 6.7 and 6.8) and/or as part of landscaping (Figure 6.9). Unfortunately, ARGD material is also used as fill (from a quarry) by uniformed contractors, such as observed at the marina on Harrison Lake, British Columbia (Figure 6.10).

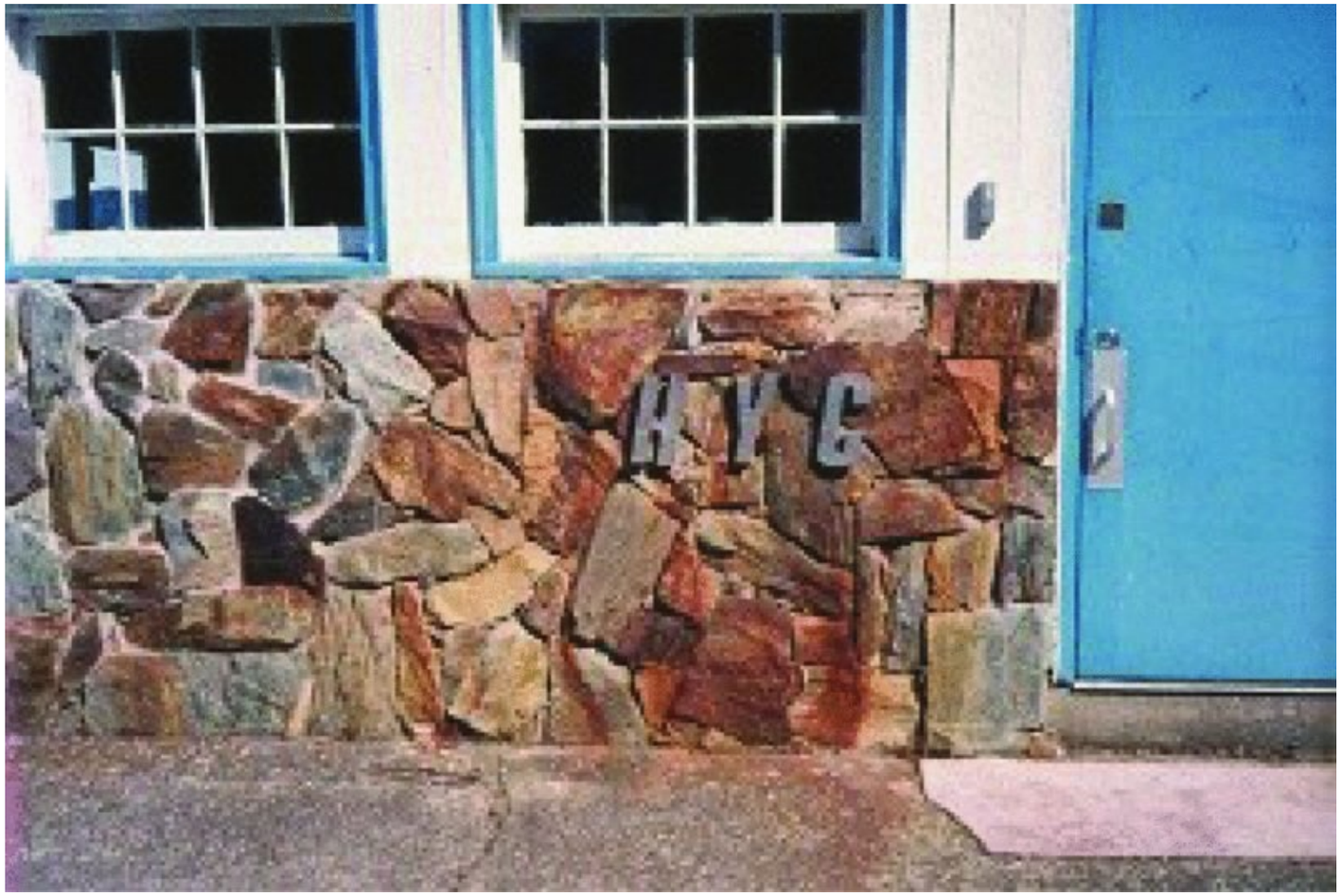

FIGURE 6.7 Decorative gossan discoloration on building stone, Harrison Lake, British Columbia, Canada.

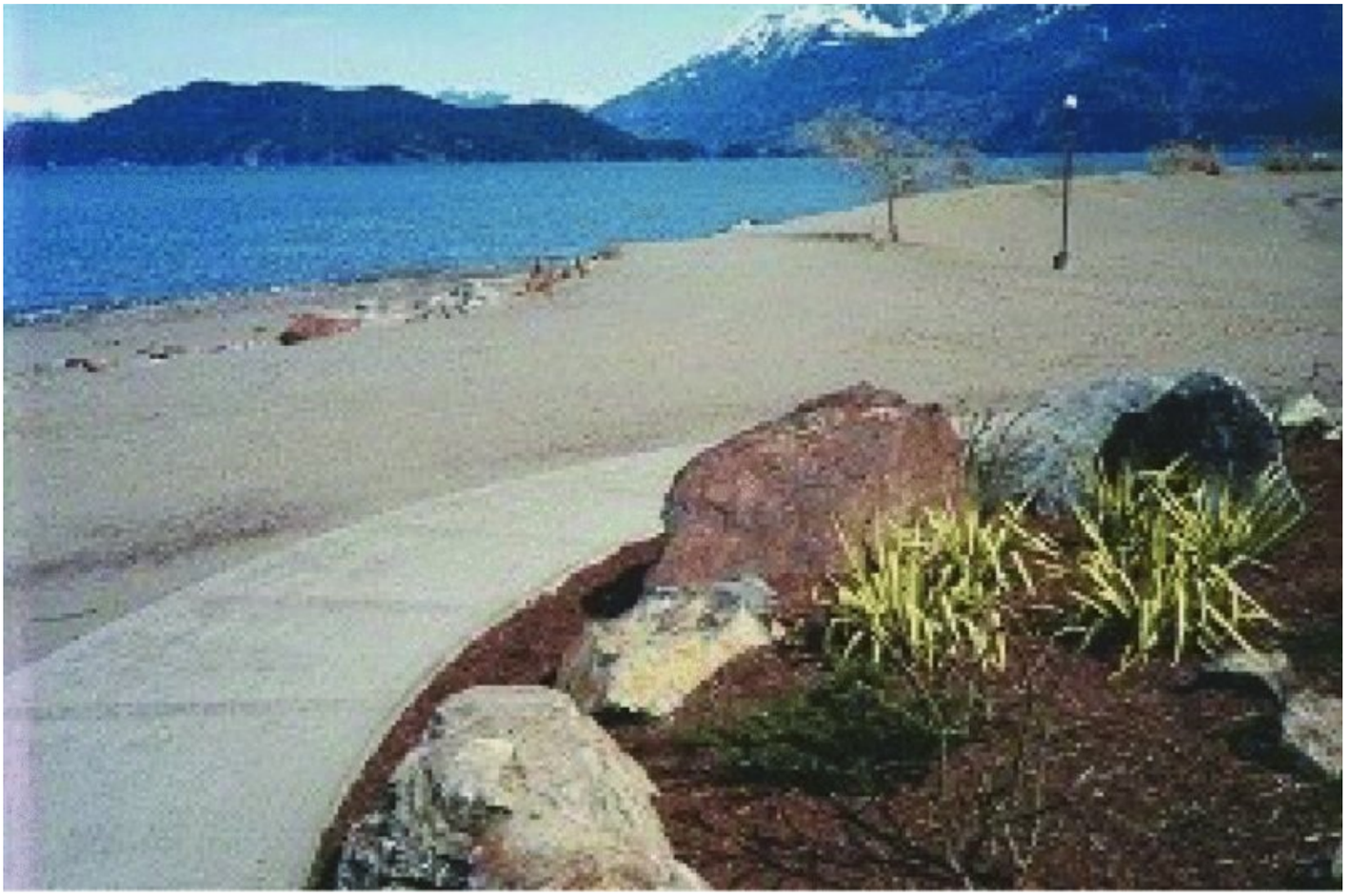

FIGURE 6.8 Gossan boulder material used as part of landscaping, Harrison Lake, British Columbia, Canada.

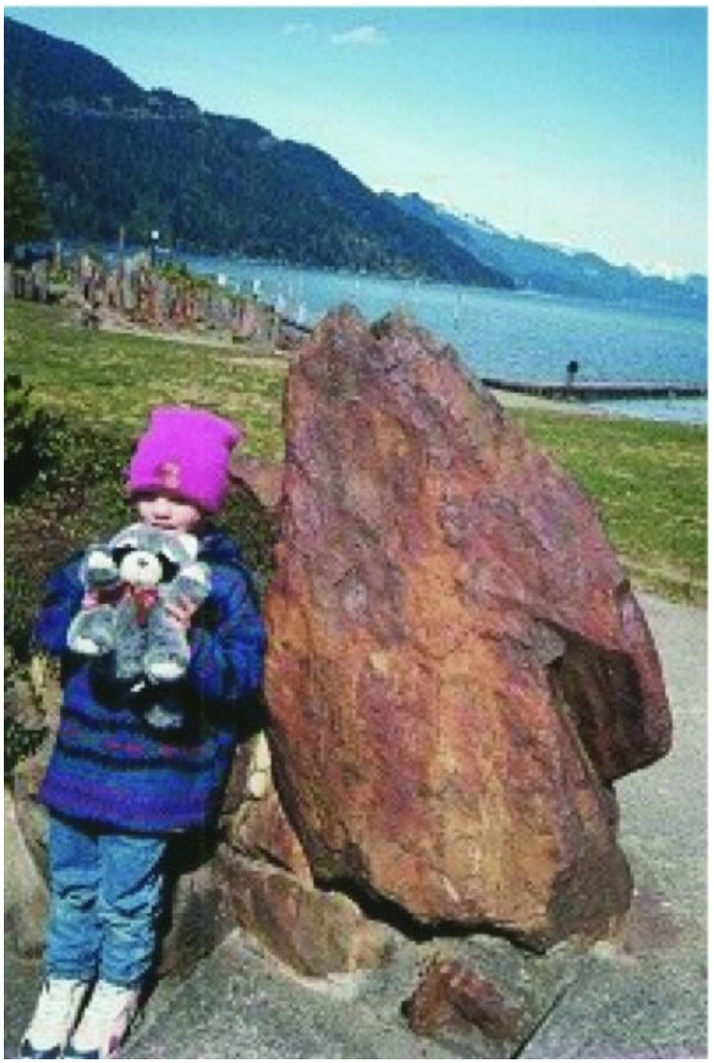

FIGURE 6.9 Gossan boulder material used as part of landscaping, Harrison Lake, British Columbia, Canada.

FIGURE 6.10 Gossanous material used as fill, Harrison Lake, British Columbia, Canada.

Supergene Mineralization

Supergene processes, kinetics and mineralization have been discussed in several papers, to which the reader is referred (Guilbert et al., 1980; Anderson, 1981; Brimhall et al., 1985; Ague and Brimhall, 1989). Supergene and surficial ore deposits, textures, and fabrics have been discussed by several authors in the third volume of an ore deposits series (Wolf, 1976). As an aside, heap leaching processes (anthropogenic) are similar to supergene (natural heap leach) processes, in that ore and gangue mineralogy are probably the parameters that most affect operating costs and recoveries. Both anthropogenic and natural heap leach usually involve similar bacterial strains with bacterial cultures from a surrounding natural ARGD environment used in anthropogenic heap leaching. A recent patent (Harlamovs et al., 2004) makes reference to the use of an acid mine drainage solution containing indigenous microorganisms for use in zinc heap leaching. The single most important difference between these two “heap” leaching processes is time. Heap leach processes are discussed in numerous publications (Dreier, 1999).

A good summation of the supergene processes has been provided by Ney et al. (1976). Supergene (secondary) mineralization is formed from metals (occurring in the host rock) transported in oxidized vadose (meteoric) water that moves primarily downward through porous and permeable material, although lateral movement can be substantial in rugged terrain. In environmental terms this process is termed *metal leaching*. In contrast, hypogene (primary) mineralization refers to the primary sulfides and oxides formed from metals transported in generally ascending hydrothermal solutions. Supergene

enrichment results in substantial reconcentration of metal values, consisting essentially of the selective replacement of primary sulfides by secondary sulfides, and to a lesser extent by the filling of interstices by oxide minerals, in the zone below the water table where oxygenated and acid leach solutions are reduced and neutralized. This process generally involves leaching of a large volume of rock and provided that the conditions at depth are favorable, metals can be redeposited at a higher grade in a smaller volume of rock. There are varying degrees of metal leaching with respect to the concentrations of metals vertically and laterally, which implies multistage enrichment.

Supergene-enriched zones can range from a few meters to over 200 m in thickness and generally have a hematitic leached cap up to tens of meters in thickness. Supergene oxidation and leaching of (1) copper-bearing intrusions (porphyry) give rise to chalcocite enrichment that forms some of the richest and largest copper deposits in the world (Perello, 1999), and (2) zinc sulfides give rise to hemimorphite and smithsonite enrichment that forms rich nonsulfide supergene deposits throughout the world (Hitzman et al., 2003), such as the Skorpion deposit (Borg et al., 2003).

During the supergene processes, there is an increase in acidity and increased content of heavy metals and sulfates in surface waters and groundwaters. Essentially, it is supergene alteration of primary hypogene mineralization which leads to natural contamination of the local environment. The supergene processes generally produce pronounced mineral zonation. The formation of oxide- and supergene-enriched mineralization may be derived from such primary mineralization types as porphyry copper, nickel–sulfide-bearing ultramafics (from which some nickel–iron laterites are formed), iron, zinc–lead–silver (Sangameshwar, 1983), gold (Butt, 1988), and manganese (Nimfopoulos et al., 1997). The zoning and paragenesis of the copper oxide, sulfide, and iron minerals may be used to assess the maturity of supergene metal enhancement. Relict-enriched blankets (or beds) may occur high in the zone of oxidation, which can subsequently be destroyed through further leaching, resulting in the creation of a new supergene-enriched zone. This natural leaching at the Earth's surface may result in plant and aquatic life being nonexistent due to metal poisoning, or being of low diversity but thriving for species able to adapt to the present conditions.

A study of supergene processes by Martycak et al. (1994) showed the importance of understanding the migration of heavy metals from ore into the adjacent environment, known generally as *geochemical dispersion*. This study involved pore solutions from which the authors were able to characterize the environment where heavy metals were released primarily into their adjacent surroundings, which affected the quality of surface water, groundwater, and soils. Geochemical dispersion will vary in metal composition and metal concentration with time and is dependent on the paleoclimate.

Various processes and substances involved in the creation of leached outcrops (leach cap, i.e., oxide zone) are discussed in detail by Blanchard (1968). The significance of leached material is paramount to understanding acid rock generation and drainage of natural and anthropogenic sulfide-bearing material and the various types of leach products. Various types of sulfides and sulfide-bearing material that oxidize under differing climatic conditions will generate different types of limonite. Limonite is the end product of iron oxidation and may occur in situ or as transported limonite. Oxidation can occur at or near the surface as well as several tens of meters in depth due to structural controls such as faults. The impurities (trace elements) both in the sulfides and in gangue influence the geochemistry of the environment arising from the oxidation reactions.

The amount of metal actually lost from the hypogene to the leached zone and into the supergene-enriched zone cannot always be readily estimated; however, if preserved material is available, a mass balance analysis can be attempted. In a study of the La Escondida mine in Chile, Alpers and Brimhall (1989) examined the present-day mineralogy in conjunction with acid rock drainage chemical processes and

were able to reconstruct the paleohydrologic and chemical evolution of a well-developed supergene ore-forming system. Various people have attempted to calculate the amount of erosion and leaching involved in producing a supergene zone such as that occurring at the La Escondida deposit in Chile (Mote et al., 2001a) and at the El Salvador deposits in Chile (Brimhall et al., 1985; Mote et al., 2001b). A study of limonite mapping within the leached capping at the La Escondida deposit permits reconstruction of the paleohydrologic and chemical evolution of a well-developed supergene ore-forming system (Alpers and Brimhall, 1989). The aerial extent of such a major porphyry deposit may cover several kilometers, with its vertical depth in excess of several hundreds of meters. This large mineralized mass has affected surface water and groundwaters for many kilometers.

A great variety of minerals are produced through the sequence of events from initial weathering to supergene development. By-products of ARGD include the formation of various iron oxides, some of which are known as yellow, brown, or red ochre and which have been used by humans as a coloring agent or pigment; malachite and turquoise are used for jewelry.

Acid Rock Generation and Drainage Through Time

Historical ARGD may be defined as geochemical processes that lead to the development of acid rock generation and drainage throughout geological time. The conceptual sequences of acid rock generation and drainage leading to supergene mineralization and related deposits are shown diagrammatically in Figures 6.1 to 6.4. Figure 6.1 is a conceptual diagram showing the vertical and lateral weathering zonation and development of the hypogene material to form various ARGD-related deposits. The processes of oxidation and enrichment are long-lived and commonly repeated over time. They are controlled by climatic conditions, tectonics, levels of erosion, the mineralogy of surrounding lithologies, and the level of the water table. Although most ARGD occurs at or near the surface, it is a process that can occur at depth with acidic groundwater percolating fractures and faults, resulting in alteration of host lithologies and mineral precipitation (i.e., gypsum) along these structures.

In geological time, the landscape can be subjected to several periods of laterite and supergene processes. The weathering and acid rock generation and drainage cycle of mineralization will have an impact on the landscape and geochemistry of the environment. Unprecedented changes due to climate change will have an impact on the permafrost landscape, which can lead to accelerated ARGD in temperate regions. Lateritic landscape in the Amazon region (da Costa, 1997) was subjected to at least two important periods of laterite (with supergene) formation, the older (Eocene to Oligocene) with development of mature laterites, and the younger (Pleistocene) leading to the development of immature laterites. Each period resulted in the development of ore deposit formation, with a corresponding impact on the geochemistry of the surrounding drainage.

Changing climatic conditions (e.g., temperature, precipitation) will affect the rate of ARGD, which can vary from month to month, year to year, and decade to decade. Butt (1997) discusses landscape models that describe the genesis and total geochemistry of the landscape, which may have an impact on ARGD and metal leaching (geochemical dispersion). The timing of surficial ore deposit weathering and development can also be used to evaluate paleoclimates and paleolandscapes.

Radiocarbon dating of ferricrete can provide a record of natural ARGD with subsequent paleoclimatic changes (Furniss et al., 1999). The formation of oxide and supergene deposits may be dated using conventional radiometric techniques on minerals within these deposits and from geology both interpreted and inferred. The age of supergene oxidation and enrichment in the Chilean porphyry copper province has been demonstrated by the dating of alunite (Sillitoe and McKee, 1996). The results indicated that

supergene processes were active from the early Oligocene (35 million years B.P.) to the middle Miocene (15 million years B.P.), a period of 20 million years. Supergene activity at individual deposits lasted for at least 0.4 to 6.2 million years. Dating of exotic mineralization at the El Salvador deposit indicates that mineralization started during the Eocene–Oligocene and continued through to the middle Miocene (Mote et al. 2001a). Darke et al. (1997) describe supergene mineralization at the Kori Kollo gold mine in Bolivia, which began around 11 Ma (and possibly up to 15 Ma ago) and that supergene alteration lasted until around 4 Ma, covering a period of at least 7 million years. Sillitoe and Lorson (1994) describe the supergene oxidation of the epithermal gold–silver–mercury deposits at Paradise Peak, Nevada. These deposits range in depth from 60 to 250 m with a sample of supergene alunite of K-Ar age 10.0 ± 0.5 Ma.

There are numerous examples of present-day in situ oxide and supergene development in environments ranging from arid to tropical to temperate climatic conditions. The Plesyumi copper prospect, Papua New Guinea, is an example of present-day oxide–supergene development which began essentially some 250,000 years ago (Titley, 1978). The Windy Craggy massive copper sulfide deposit (Claridge and Downing, 1991) is an example of oxide–supergene development under temperate conditions where the supergene development is occurring essentially at the present time, resulting in potentially minable reserves (Downing and Giroux, 1993) Present-day mine waste dumps will essentially form oxide caps with minor supergene development and could become economically minable in future millennia. Gossans can form today and have formed over geologic time (sometimes up to several tens of thousands of years) and may form mineral-enriched mantos or supergene zones. A similar process occurs at many mines where dump leaching is used, or at waste and tailings dumps where natural leaching is prominent (Chermak and Runnells, 1997). The time period of these investigations indicate the perpetuity of ARGD development.

Natural Metal Concentrations

A literature review of current ARGD research indicates a frequent lack of understanding of trace element geochemistry (Downing and Mills, 1998) and lithogeochemistry (Downing and Madeisky, 1999) with respect to ARGD. Metal concentrations in the environment are dependent on variations of metal content in naturally occurring media (i.e., bedrock, soil), and a knowledge of local and regional geochemical processes can lead to a better understanding of the impact of metals on the environment. It can also provide technical constraints on environmental regulations which should be incorporated into the regulatory process. Here we deal only with natural (background) ARGD and do not consider anthropogenic sources.

A report by the Geological Survey of Canada (Reichenbach, 1993) indicates how black shales can be considered to be environmentally hazardous in Canada. Black shales commonly host complex assemblage of elements that have a significant influence on the environment. A major area of Devonian–Mississippian black shale area covering several hundred square kilometers in northeastern British Columbia and the Yukon is acid generating. The acid produced by these shales is natural, not a product of mining. It is also a natural process to which the environment has adjusted. Reports by Kwong and Whiteley (1992a,b) describe natural acid rock drainage at McMillan Pass, Yukon. Based on measurements of 12 parameters, the criteria for drinking water and aquatic life failed to meet acceptable standards. Studies carried out by the British Columbia Geological Survey (Koyanagi, 1994; Koyanagi and Panteleyev, 1994) on northern Vancouver Island demonstrated the source and extent of natural acidity in waters draining areas of altered and mineralized rock. Results of sampling and analyzing streams throughout British Columbia have identified over 100 occurrences of natural acid generation (Price and Errington, 1995). Other studies on natural ARGD and natural metal leaching have been conducted by Mast et al. (2000), Posey et al. (2000),

and Yager et al. (2000). Natural ARGD and ML are becoming more recognized and documented.

Metals can be present in various media as inorganic and organic complexes, colloids, adsorbed on colloids, adsorbed on inorganic and organic material or precipitates, or incorporated within biological materials. Speciation is complex and dependent on temperature, pH, dissolved oxygen, concentration, and other factors. Examination of Eh–pH diagrams indicates the complexity of metal speciation (Garrels and Christ, 1965). Both total and dissolved metals must be taken into account because the chemical species of a particular metal can have different impacts on aquatic organisms (i.e., bioavailability). A study by Taufen (1997) on groundwater and surface waters examined solution speciation, mineral precipitation, and element sorption onto solid subtrates and solution particulates and concluded that the free-ion forms of metals are much more toxic to aquatic life than are the same metals in the form of metal-complexed species.

Natural waters are multicomponent electrolyte solutions. A study by Williamson and Parnell (1994) demonstrates the use of selective, sequential extraction of metals from lake sediments and its implications for selective metal remobilization under variable environmental conditions, both natural and anthropogenic. This has a direct bearing on natural background metal concentrations which should be taken into consideration in project baseline assessment and environmental permitting. The closure plan for the Bell mine in British Columbia recognizes copper complexing and the importance of the complexing capacity of Babine Lake and Hagen Arm (Singleton, 1987; Noranda Minerals, 1992).

Variations in the composition of biota and water are influenced by soils, which, in turn, are dependent on the geochemical nature of bedrock. In an article by Logan and Traina on metals in agricultural soils (Allen et al., 1993), the authors observe that the interaction of soil with surface water and groundwater is a fundamental process controlling the solubility of trace metals in water and their impact on water and soil quality. The biogeochemistry of metals in natural aquatic systems is complex. Principles and concepts of metal biogeochemistry in surface water systems are discussed by Elder (1988), and the natural geochemistry of the environment is discussed in detail in many publications, including *Environmental Geochemistry* by Fortescue (1980) and *The Natural Geochemistry of Our Environment* by Speidel and Agnew (1982). Thorton et al. (1983) discuss the interaction between geochemical and pollutant metal sources in the environment and the implications for the community.

There are various definitions of the term *background*. In the mineral and mining industry, background is defined as “the abundance of an element or any chemical property of a naturally occurring material in areas where the chemical pattern has not been affected by the presence of a mineral deposit” (Thrush, 1990). Also: “The natural background of a metal in the environment can be defined as the metal fraction that originates from natural geological, biogeochemical and other processes” (Metals Environmental Risk Assessment Guidance, 2007). In geochemical exploration terms, background is defined as “the abundance of an element, or any chemical property of a naturally occurring material, in an area in which the concentration is not anomalous” (Bates and Jackson, 1987). Because background concentrations vary, statistical analyses should be undertaken to calculate the background and the threshold and anomalous values (Fletcher et al., 1986; Reimann et al., 2005). Each medium will have its own natural background and threshold values. For the purpose of identifying contaminated sites, elevated metal concentrations associated with mineral deposits can be considered part of the range of natural variability in element concentrations.

Natural background concentrations of elements in the environment are dependent on interactions between rock, soil, water, and vegetation. If the dominant source of the parent material is nonmineralized and unaltered, metal concentrations tend to be low. If the source is mineralized and/or altered, higher levels of elemental concentrations can be expected. Mineralized areas include both metallic and nonmetallic

minerals. These levels can be measured from baseline studies around specific sites determined by regional geochemical mapping programs, such as the stream sediment surveys (sponsored by both the federal and provincial governments in Canada). Concentrations of substances in soil, stream and lake sediments, and water are dependent on both the local geological and biological environments within specific drainage basins and cannot be used as overall standards because they may be different for each drainage basin, compared with or measured against the values for the regional landscape.

The natural range and variability of regional element concentrations in geologic material is dependent on the local environment. Tables of elemental concentrations are available for a variety of environmental matrices, but these are generally from nonmineralized sites. Crustal average abundances, known as *Clarke values* (Clarke, 1924), for various elements has been used as a measure of background. Global geochemical databases are becoming available for many areas of the world (Darnley et al., 1995). Some caution should be exercised in using these values, however, since secondary iron and manganese oxides, which are “strong scavengers” for many heavy metals released during the weathering process, have an impact on the natural background concentrations of some metals (Jenne, 1968).

Government geochemical data (stream and lake sediment) should be used by regulatory agencies to develop a set of area-specific background and acceptable metal levels. Painter et al. (1994) have published several maps covering various areas of Canada, in which they show natural background levels for eight elements. They discuss the importance of reconnaissance geochemistry and its environmental relevance. They note that the concentrations of metals in the natural environment vary widely, and in some areas unaffected by human activity may reach levels that elsewhere have been considered to have an effect on the ecosystem. Thorton et al. (1983) suggested using stream sediments as an estimate of trace element concentrations for water that could be useful in the selection of critical sites for routine water sampling.

Naturally occurring “contaminated” sites in British Columbia, Canada, can be compiled through review of the public database. There are in excess of 11,375 documented naturally occurring mineralized sites throughout British Columbia (MINFILE), of which approximately 400 are coal, 600 industrial minerals, and 10,000 base and precious metals. Most of these sites would be classified as “contaminated sites” under British Columbia's contaminated sites regulations.

Metal concentrations in soil and water exert a strong influence on vegetation. The recognition of residual versus transported soils is equally important for metal concentrations. After a two-year study on the biogeochemistry of copper and cadmium in two different ecosystems, Keller et al. (1992) concluded that soil properties are more important for determining the movement of metals in soil than are the properties of metals themselves. Variations in metal content are also associated with different levels of soil classification. A geochemical survey of some soils in Missouri (Tidball, 1976) shows that the variation of element concentrations between soil series is much larger than the variation within a given series. A study of plant uptake of heavy elements as a function of element speciation shows the necessity of understanding metal species availability and the method of analysis (Dunn, 1989). The distinction between “total metal” and “available metal” is critical to an understanding of potential pollution and contamination problems. Plant stress may occur, resulting in nonvegetated (i.e., “kill”) zones if there is natural contamination. Recognizing stressed plant communities is a technique used by explorationists to identify potential mineralized areas.

Natural background metal concentrations vary with lithological boundaries. Differences also exist within lithologically similar bedrock. Since lithological boundaries do not coincide with political or administrative boundaries, the standards for maximum acceptable concentrations in particular media should be consistent for all provinces and states and/or should be adjusted according to lithological

boundaries.

Geoenvironmental Models

As ARGD is controlled essentially by bedrock geology, an understanding of the geological and geochemical environments is extremely important. Conceptual models for ore formation and mineralization provide the ARGD practitioner and regulator with some ideas as to the potential impact of metal leaching and mobility from both a natural and an anthropogenic context. An understanding of ore deposit models is basic in determining the natural background values that reflect the primary character of the mineralization and alteration. The geoenvironmental concept is discussed in published papers by Alpers and Nordstrom (2000) and Kwong (2003).

Anomalous concentrations of elements are of importance to exploration geologists and geochemists because they generally indicate mineralization that is the source of anomalous values. There is no universal standard for anomalous values or concentrations because they are dependent on the area or region and medium that is sampled and on statistical determinations of the background and threshold concentration levels. Anomalous values, which may ultimately lead to the development of a mine, may be several orders of magnitude higher than those presently accepted by various government departments as maximum acceptable concentrations for certain uses and activities. A study by Bradshaw (1975) of several mineral deposits in British Columbia outlined the use of natural background and anomalous element concentrations, in various media, in locating the deposits with respect to the region in which they occur. Sutherland-Brown (1973) described the variation of natural metal concentrations of five regional tectonic belts in British Columbia in terms of potential mineral exploration.

Ficklin et al. (1992) attempted a geochemical classification of mine and natural drainages in mineralized areas. Their conclusions indicate that natural drainages in mineralized areas produce waters that are chemically similar to mine drainage waters. The maximum acceptable concentrations of substances found in many government regulations are based on land-use classifications and do not take into account the natural background variations based on bedrock and Quaternary media. There is a geological background variation that influences these concentrations.

Determining the “natural” levels of metals and other solutes in surface waters and groundwaters and soils is a prerequisite to planning a mine development. Remediation standards, which can be based on rather rigid guidelines (e.g., aquatic toxicity, drinking water, or agricultural standards), may be unrealistic because they ignore the natural geochemical character of mineralized areas before and after mining. Determination of natural background concentrations of dissolved components in water at mining, milling, and smelting sites has been investigated by Runnells et al. (1998), Alpers and Nordstrom (2000), and Davis et al. (2000). ARGD prediction and treatment are the subject of substantial research efforts by governments, the mining industry, universities, and independent research establishments.

Conclusions

Supergene processes have not been recognized as an acid rock drainage process by most ARGD practitioners, regulators, environmentalists, and the public. Few geologists interpret geology with respect to acid rock generation processes, and environmental practitioners do not interpret ARGD and ML as geological and geochemical processes.

The concept of acid rock drainage as a natural “perpetual reaction process” has a long-range effect on the environment, implied in the “mother nature” and anthropogenic perpetual care statements for ARGD sites.

The impact of historical acid rock drainage is immense, as observed in the tonnages of mineralized material reported (Table 6.1), which would have had a major impact on the environment, geochemistry, and biotic life. The effects we observe today with respect to ARGD have certainly occurred in the geological past. It might be appropriate to conclude that low-grade waste dumps (anthropogenic acid rock generation) could, in fact, become mineral-enriched (supergene) with geological time. The effects of ARGD have economic benefits or costs, depending on the time frame in which they are viewed. The environment and landscape geochemistry adapts to changing conditions throughout geological time.

Generally, ARGD studies should be initiated during the exploration stage and continue during mining operations, reclamation, and post-closure monitoring in order to characterize natural sources of ARGD and anthropogenic sources. This will also allow the environmental practitioner to perform accurate risk assessments for metals from the natural surroundings. Understanding the potential for ARGD is recognized as a key component of mine planning, waste rock disposal, and reclamation. The primary objective of this planning is to reduce and control ARGD through proper handling and disposal of the rock most at risk of generating ARGD. The intention in this chapter has been to make the public, regulators, and environmental practitioners aware of the need to interpret ARGD with respect to naturally occurring events throughout geological time of a mineralized region's evolution from formation to reclamation and to be cognizant of the environmental impact(s) related to natural background geochemistry.

Acknowledgment

I would like to thank my colleagues for their time in reading various versions of the chapter. I am aware that numerous other examples of natural ARGD and ML sites exist but are not documented in the published literature.

References and Suggested Reading

Ague, J.J., and Brimhall, G.H., 1989. Geochemical modeling of steady state fluid flow and chemical reaction during supergene enrichment of porphyry copper deposits. Economic Geology, vol. 84, pp. 506–526.

Allen, H.E., Perdue, E.M., and Brown, D.S., 1993. Metals in Groundwater. CRC Press/Lewis Publishers, Boca Raton, FL.

Alpers, C.N., and Brimhall, G.H., 1989. Paleohydrologic evolution and geochemical dynamics of cumulative supergene metal enrichment at La Escondida, Atacama desert, northern Chile. Economic Geology, vol. 84, no. 2, pp. 229–255.

Alpers, C.N., and Nordstrom, D.K., 2000. Estimation of pre-mining conditions for trace metal mobility in mineralized areas: an overview. In: Proceedings of the 5th International Conference on Acid Rock Drainage, Society for Mining, Metallurgy, and Exploration, Englewood, CO, pp. 463–472.

Anderson, J.A., 1981. Characteristic of leached capping and techniques of appraisal. In: Advances in Geology of the Porphyry Copper Deposits, Southwestern North America, R. Titley, ed. University of Arizona Press, Tucson, AZ, pp. 275–296.

Bates, R.L., and Jackson, J.A., eds., 1987. Glossary of Geology, 3rd ed. American Geological Institute, Alexandria, VA.

Blanchard, R., 1968. Interpretation of Leached Outcrops. Bulletin 66, 215 pp. Nevada Bureau of Mines, Reno, NV.

Borg, G., Karner, K., Buxton, M., Armstrong, R., and van der Merwe, S.W., 2003. Geology of the Skorpion supergene zinc deposit, southern Namibia. Economic Geology, vol. 98, no. 4, pp. 749–771.

Bradshaw, P., 1975. Conceptual models in exploration geochemistry. Journal of Geochemical Exploration, special vol. 4, no. 1, pp. 15–106.

Brimhall, G.H., Alpers, C.N., and Cunningham, A.B., 1985. Analysis of supergene ore-forming processes and ground-water solute transport using mass balance principles. Economic Geology, vol. 80, no. 5, pp. 1227–1235.

Brooks, R.R., 1972. Geobotany and Biogeochemistry in Mineral Exploration, Harper & Row, New York.

Butt, C.R.M., 1988. Genesis of supergene gold deposits in the lateritic regolith of the Yilgarn Block, Western Australia. In: The Geology of Gold Deposits: The Perspective in 1988. Economic Geology Monograph 6, pp. 460–470.

Butt, C.R.M., 1997. Regolith landform-based geochemical dispersion models. In: Exploration Geochemistry of Tropical Environments. Mineral Deposit Research Unit Short Course 21. Deptartment of Earth and Ocean Sciences, University of British Columbia, Vancouver, BC, Canada.

Camus, F., Silitoe, R.H., and Peterson, R., eds., 1996. Andean Copper Deposits: New Discoveries, Mineralization and Metallogeny. Special Publication 5. Society of Economic Geologists, Littleton, CO, 198 pp.

Chermak, J.A., and Runnells, D.D., 1997. Development of chemical caps in acid rock drainage environments. Mining Engineering, June, pp. 93–97.

Claridge, P., and Downing, B.W., 1991. Environmental geology and geochemistry of the Windy Craggy massive Cu–Co–Au–Ag–Zn sulphide deposit, British Columbia. CIMM Bulletin, vol. 86, no. 966, 50–57.

Clark, F.W., 1924. The Data of Geochemistry. Bulletin 770. U.S. Geological Survey, Reston VA.

Coulter, D., 2006. Remote Sensing Analysis of Alteration Mineralogy Associated with Natural Acid Drainage in the Grizzly Peak Caldera, Sawatch Range, Colorado. Ph.D. dissertation. Colorado School of Mines, Golden, CO.

da Costa, M.L., 1997. Laterization as a major process of ore deposit formation in the Amazon region. Exploration and Mining Geology, vol. 6, no. 1, pp. 79–104.

Darke, K.E., Boyce, A.J., Clapperton, C.M., Fallick, A.E., Redwood, S.D., and Rice, C.M., 1997. Supergene mineralization at the Kori Kollo gold mine, Bolivia. Exploration and Mining Geology, vol. 6, no. 3, pp. 209–222.

Darnley, A.G., Bjorklund, A., Bolviken, B., Gustavsson, N., Koval, P.V., Plant, J.A., Steenfelt, A., Tauchid, M., Xuejing, X., Garrett, R.G., and Hall, G.E.M., 1995. A Global Geochemical Database for Environmental and Resource Management. Final report of IGCP Project 259. UNESCO, Paris.

Davis, A., Tisdale, A., and Byrns, C., 2000. Discriminating between background and mine-impacted waters. In: Proceedings of the 5th International Conference on Acid Rock Drainage. Society for Mining,

Metallurgy, and Exploration, Englewood, CO, pp. 473–484.

Downing, B.W., and Giroux, G., 1993. Estimation of a waste rock ARGD block model for the Windy Craggy massive sulphide deposit, northwestern British Columbia. Exploration and Mining Geology, vol. 2, no. 3, pp. 203–215.

Downing, B.W., and Madeisky, H.E., 1999. Lithogeochemical methods for acid rock drainage studies and prediction. Exploration and Mining Geology, vol. 6, no. 4.

Downing, B.W., and Mills, C., 1998. Trace Element Geochemistry in Acid Rock Drainage, http://technology.infomine.com/enviromine/ard/. Published on the ARD website, www.enviromine.com/ard.

Dreier, J., 1999. Geochemical aspects of copper heap leaching. In: Copper 99/Cobre 99, October 10–13, Phoenix, AZ.

Dunn, C., 1989. Developments in biogeochemical exploration. In: Proceedings of Exploration ’87, Ontario Geological Survey, special vol. 3, p. 417.

Elder, J.F., 1988. Metal Biogeochemistry in Surface-Water Systems: A Review of Principles and Concepts. Circular 1013, U.S. Geological Survey, Reston, VA.

Ficklin, W.H., Plumlee, G.S., and McHugh, J.B., 1992. Geochemical classification of mine drainages and natural drainages in mineralized areas. In: Proceedings of the 7th International Symposium on Water–Rock Interaction, Park City, UT.

Fletcher, W.K., Hoffman, S.J., Mehrtens, M.B., Sinclair, A.J., and Thomson, I., 1986. Reviews in Economic Geology, vol. 3. Society of Economic Geologists, Littleton, CO.

Fortescue, J.A.C., 1980. Environmental Geochemistry: A Holistic Approach. Springer-Verlag, New York.

Furniss, G., Hinman, N.W., Doyle, G.A., and Runnells, D.D., 1999. Radiocarbon-dated ferricrete provides a record of natural acid rock drainage and paleoclimatic change. Environmental Geology, vol. 37, no. 1–2, pp. 102–106.

Gamah International Ltd., 1997. World Copper Deposits and Production Database. Sameh, Toronto, ON, Canada.

Garrels, R.M., and Christ, C.L., 1965. Solutions, Minerals and Equilibria. Freeman, Cooper, San Francisco.

Grant, W.H., 1969. Abrasion pH: an index of chemical weathering. Clays and Clay Minerals, vol. 17, pp. 151–155.

Guilbert, J.M., and Park, C.F., Jr., eds., 1980. Supergene sulphide enrichment. In: The Geology of Ore Deposits. Waveland Press, Long Grove, IL, pp. 796–836.

Harlamovs, J.R., Ashman, D.W., Gonzalez, J.A., Lizama, H.M., Makwana, D.D., and Stradling, A.W., 2004. Heap bioleaching process for the extraction of zinc. U.S. Patent 6,736,877.

Hitzman, M., Reynolds, N.A., Sangster, D.F., Allen, C.R., and Carman, C.E., 2003. Classification, genesis, and exploration guides for non-sulphide zinc deposits. Economic Geology, vol. 98, no. 4,

pp. 685–714.

Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. Advances in Chemistry Series, vol. 73, pp. 337–388.

Keller, C., Domergue, F.L., and Vedy, J.C., 1992. Biogeochemistry of copper and cadmium in unpolluted forests. In: Impact of Heavy Metals on the Environment, Trace Metals in the Environment, vol. 2, J.-P. Vernet, ed. Elsevier, Amsterdam, pp. 247–271.

Koyanagi, V.M., and 1994. Northern Vancouver Island geology and related acid rock drainage. Presented at the 2nd Annual British Columbia Acid Rock Drainage Symposium, British Columbia Geological Survey, British Columbia Ministry of Energy, Mines and Petroleum Resources, Vancouver, BC, Canada.

Koyanagi, V.M., and Panteleyev, A., 1994. Natural Acid Rock Drainage in the Red Dog–Hushamu–Pemberton Hills Area, Northern Vancouver Island (92L/12). Geological Fieldwork 1993, Paper 1994-1. British Columbia Geological Survey, Vancouver, BC, Canada.

Kwong, Y.T.J., 2003. Comprehensive environmental ore deposit models as an aid for sustainable development. Exploration and Mining Geology, vol. 12, no. 1–4, 1–4.

Kwong, Y.T.J., and Whiteley, W.G., 1992a. Natural Acid Rock Drainage at Macmillan Pass. Yukon DIAND MEND Project 11, NHRI Contribution 92046. MEND, Ottawa, ON, Canada.

Kwong, Y.T.J., and Whiteley, W.G., 1992b. Heavy metal attenuation in northern drainage systems. Presented at the International Northern Research Basins Symposium/Workshop, Canada.

Laughlin, W.P., 1991. Principal component analysis for alteration mapping. Engineering and Remote Sensing, vol. 57, no. 9, pp. 1163–1169.

Martycak, K., Zeman, J., and Vacek-Vesely, M., 1994. Supergene processes on ore deposits: a source of heavy metals. Environmental Geology, vol. 23, pp. 156–165.

Mast, M., Verplanck, P.J., Yager, D.B., Wright, W.G., and Bove, D.J., 2000. Natural sources of metals to surface waters in the Upper Animas River watershed, Colorado. In: Proceedings of the 5th International Conference on Acid Rock Drainage. Society for Mining, Metallurgy, and Exploration, Englewood, CO, pp. 513–533.

Metals Environmental Risk Assessment Guidance, 2007. International Council on Mining and Metals, London.

Mills, C., 1995. The role of micro-organisms in acid rock drainage: EnviroMine. http://technology.infomine.com/enviromine/ard/Microorganisms/roleof.htm.

Mote, T.I., Becker, T.A., Renne, P., and Brimhall, G.H., 2001a. Chronology of exotic mineralization at El Salvador, Chile, by 40Ar/39Ar dating of copper wad and supergene alunite. Economic Geology, vol. 96, no. 2, pp. 351–366.

Mote, T.I., Brimhall, G.H., Tidy-Finch, E., Muller, G., and Carrasco, P., 2001b. Application of mass-balance modeling of sources, pathways, and sinks of supergene enrichment to exploration and discovery of the Quebrada Turquesa exotic copper orebody, El Salvador District, Chile. Economic Geology, vol. 96, no. 2, pp. 367–386.

Munchmeyer, C., 1996. Exotic deposits: products of lateral migration of supergene solutions from porphyry copper deposits. In Andean Copper Deposits: New Discoveries, Mineralization, Styles and Metallogeny. Special publication 5. Society of Economic Geologists, Littleton, CO, pp. 43–58.

Ney, C.S., Cathro, R.J., Panteleyev, A., and Rotherham, D.C., 1976. Supergene copper mineralization, porphyry deposits of the Canadian Cordillera. CIM special vol. 15, pp. 72–78.

Nimfopoulos, M.K, Pattrick, R.A.D., Michailidis, K.M., Polya, D.A., and Esson, J., 1997. Geology, geochemistry and origin of the continental karst-hosted supergene manganese deposits in the Western Rhodope Massif, Macedonia, northern Greece. Exploration and Mining Geology, vol. 6, no. 2, pp. 171–184.

Noranda Minerals Inc. and Rescan, 1992. Bell 92 Project Closure Plan, Support Document H, Existing Environmental Conditions of Babine Lake in the Vicinity of Bell Mine. British Columbia Ministry of Environment, Victoria, BC, Canada.

Painter, S., Cameron, M., Allan, R., and Rouse, J., 1994. Reconnaissance geochemistry and its environmental relevance. Journal of Geochemical Exploration, vol. 51, pp. 213–246.

Perello, J.A., 1999. Formation of giant chalcocite blankets: lessons from the northern Chile porphyry copper belt. Abstract, Systematics of Supergene Enrichment in Bulk Mineable Deposits and Mining Applications. Presented at the SME Annual Meeting, March 1–3, Denver, CO.

Posey, H.H., Renkin, M.L., and Woodling, J., 2000. Natural acid drainage in the Upper Alamosa River of Colorado. In: Proceedings of the 5th International Conference on Acid Rock Drainage. Society for Mining, Metallurgy, and Exploration, Englewood, CO, pp. 485–498.

Price, W.A., and Errington, J.C., 1995. ARD Guidelines for Mine Sites in British Columbia. Mine Review and Permitting Branch, Ministry of Energy, Mines and Petroleum Resources, Victoria, BC, Canada.

Reichenbach, I., 1993. Black Shale as an Environmental Hazard: A Review of Black Shales in Canada. Geological Survey of Canada Open File 2697. Natural Resources Canada, Ottawa, ON, Canada.

Reimann, C., Filzmoser, P., and Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Science of the Total Environment, vol. 346, pp. 1–16.

Rosler, H.J., and Lange, H., 1972. Geochemical Tables. Elsevier, Amsterdam.

Runnells, D.O., Dupon, D.P., Jones, R.L., and Cline, O.J., 1998. Determination of natural background concentrations of dissolved components in water at mining, milling and smelting sites. Mining Engineering, February, pp. 65–71.

Sangameshwar, S.R., 1983. Supergene process in zinc–lead–silver ores in carbonates. Economic Geology, vol. 78, pp. 1379–1397.

Sillitoe, R.H., 1995. Exploration and Discovery of Base-Metal and Precious-Metal Deposits in the Circum-Pacific Region During the Last 25 Years. Metal Mining Agency of Japan, pp. 17–20.

Sillitoe, R.H., and Lorson, R.C., 1994. Epithermal gold–silver–mercury deposits at Paradise Peak, Nevada: ore controls, porphyry gold association, detachment faulting, and supergene oxidation. Economic Geology, vol. 89, pp. 1228–1248.

Sillitoe, R.H., and McKee, E.H., 1996. Age of supergene oxidation and enrichment in the Chilean porphyry copper province. Economic Geology, vol. 91, pp. 164–179.

Singleton, H.J., 1987. Water Quality Criteria for Copper (Technical Appendix). Resource Quality Section, Water Management Branch, British Columbia Ministry of Environment, Victoria, BC, Canada.

Speidel, D.H., and Agnew, A.F., 1982. The Natural Geochemistry of Our Environment. Westview Special Studies in Natural Resources and Energy Management. Westview Press, Boulder, CO.

Stevens, R.E., and Carron, M.K., 1948. Simple field test for distinguishing minerals by abrasion pH. American Mineralogist, vol. 33, pp. 1–2, 31–49.

Sutherland-Brown, A., 1973. Aspects of metal abundances and mineral deposits in the Canadian Cordillera. Abstract. CIM Bulletin, vol. 66, no.731, p. 67.

Taufen, P.M., 1997. Ground waters and surface waters in exploration geochemical surveys. In: Proceedings of Exploration ’97: 4th Decennial International Conference on Mineral Exploration, pp. 271–284.

Taylor, G.F., and Thornber, M.R., 1995. The mechanisms of sulphide oxidation and gossan formation. In: Proceedings of the 17th International Geochemical Exploration Symposium, Townsville, Queensland, Australia, pp. 115–138.

Thornber, M.T., Allchurch, P.D., and Nickel, E.H., 1981. Variations in gossan geochemistry at the perseverance nickel sulphide deposit, Western Australia: a descriptive and experimental study. Economic Geology, vol. 76, pp. 1764–1774.

Thorton, I., Abrahams, P.W., Culbard, E., Rother, J.A.P., and Olson, B.H., 1983. The interaction between geochemical and pollutant metal sources in the environment: implications for the community. In: Applied Geochemistry in the 1980's, I. Thorton and R.J. Howarth, eds. Graham & Trotman, London.

Thrush, P.W., ed., 1968. Dictionary of Mining, Mineral and Related Terms. Special Publication. U.S. Bureau of Mines, Department of the Interior, Washington, DC.

Tidball, R.R., 1976. Chemical variation of soils in Missouri associated with selected levels of the soil classification system. USGS Professional Paper 954-B. In: Geochemical Survey of Missouri. U.S. Department of the Interior, Washington, DC.

Titley, S.R., 1978. Geologic history, hypogene features, and processes of secondary sulphide enrichment at the Plesyumi copper prospect, New Britain, Papua New Guinea. Economic Geology, vol. 73, pp. 768–784.

Van der Zee, S.E., and de Haan, F.A., 1992. Soil and ground water quality indicators. In: Environmental Impact Assessment, A.G. Colombo, ed. Kluwer Academic, Dordrecht, The Netherlands, pp. 235–259.

Williamson, M.A., and Parnell, R.A., 1994. Partitioning of copper and zinc in the sediments and porewaters of a high-elevation alkaline lake, east-central Arizona. Applied Geochemistry, vol. 9, pp. 597–608.

Wolf, K.H., 1976. Supergene and surficial ore deposits: textures and fabrics. In: Handbook of Strata-Bound and Stratiform Ore Deposits, vol. 3, Elsevier, Amsterdam.

Yager, D.B., Mast, M., Verplanck, P.J., Bove, D.J., Wright, W.G., and Hageman, P.L., 2000. Natural versus mining-related water quality degradation to tributaries draining Mount Moly, Silverton, Colorado. In: Proceedings of the 5th International Conference on Acid Rock Drainage. Society for Mining, Metallurgy, and Exploration, Englewood, CO, pp. 535–547.

7
The Sulfur Cycle: Acid Drainage and Beyond

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Integral to acid mine drainage processes is the sulfur cycle (Figure 7.1). The sulfur cycle is a natural biotic and abiotic process in which energy derived from sulfur chemistry appears to play in the origin of life on Earth and potentially in extraterrestrial life as well. Sulfide oxidation, the mechanism for acid drainage, is a portion of that important sulfur chemistry that is an abundant source of energy to microbes and is also a major biochemical reaction in the changing geochemistry on Earth.

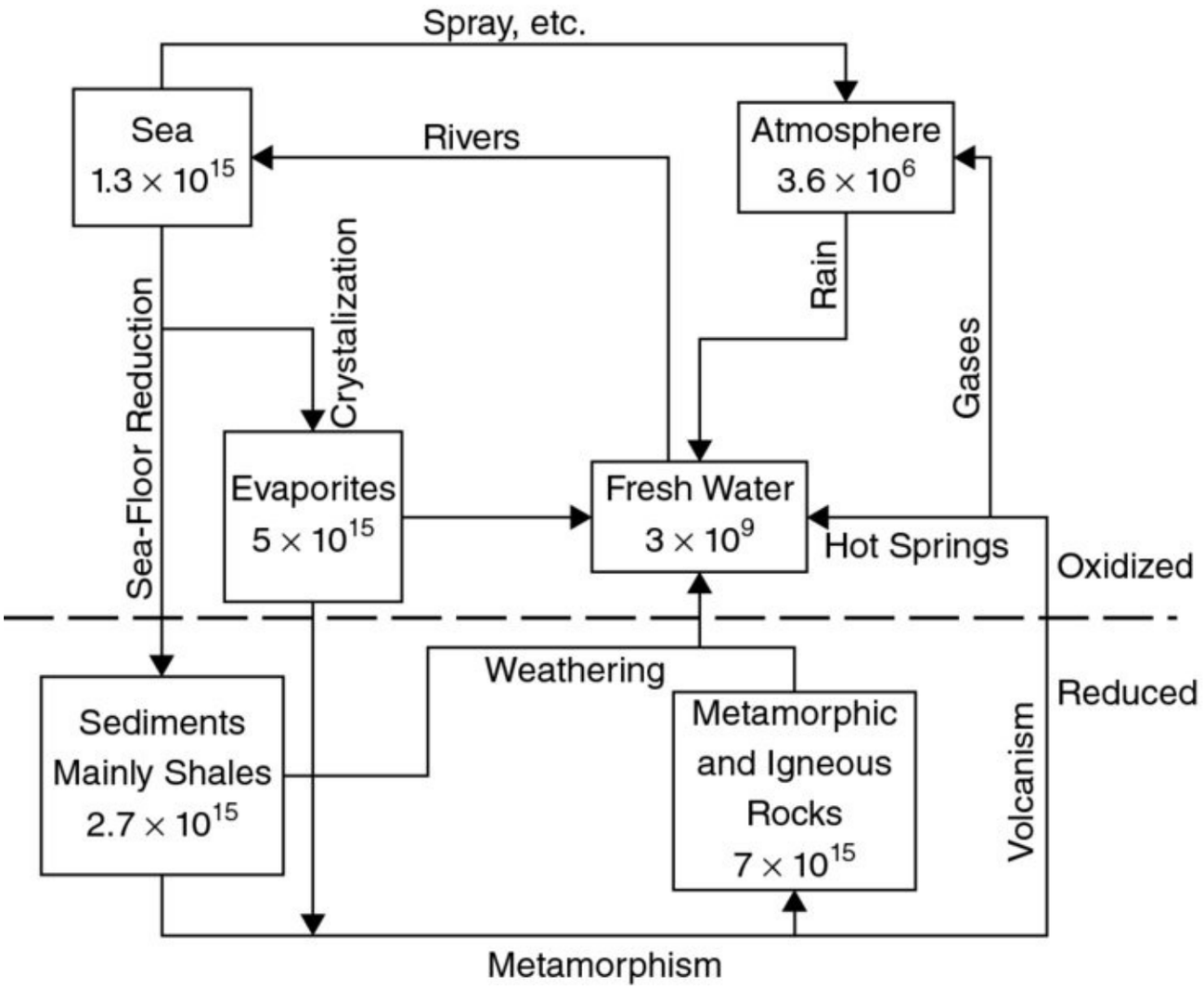


FIGURE 7.1 Global sulfur cycle, including shale deposition and metamorphic and igneous rocks. These formations are frequently disturbed during mining operations, causing AMD. (From U.S. Environmental Protection Agency, 2003.)

Some Background And Fundamentals Of Microbial Life

On Earth, most abiotic geochemical reactions are driven by the transfer of protons without electrons,

which is in essence acid–base chemistry. In contrast, the chemistry of life is based on oxidation–reduction reactions that entail the transfer of electrons and protons. Typically, microbial processes exploit chemical reactions that yield energy thermodynamically but that in many cases under abiotic conditions may have poor kinetics. Microbial utilization, the essence of life, accelerates kinetics, and the microbes derive energy in the process essentially by acting as electron transfer agents. A suitable definition here for *microbial processes* is: a self-organized consortium of complicated chemicals capable of reproducing that includes chemical pathways to extract energy from the environment (Sleep, 2010).

There are three primary kingdoms of life: (1) bacteria, (2) archaea, and (3) eukarya. Here we use the term *microbe* (or its derivatives) because bacteria and archaea appear to be similar in size and shape and were at one time both simply considered to be prokaryotes. Later it was discovered that the two have distinctly different evolutionary histories and sufficiently different internal biochemistry to justify the creation of an entirely new kingdom of life for them.

A fundamental classification of microbial life is based on energy and carbon sources (Macalady and Banfield, 2003):

- Energy from light and carbon from carbon dioxide: *photoautotroph*
- Energy from light and carbon from organic carbon: *photoheterotroph*
- Energy from inorganic chemicals and carbon from carbon dioxide: *lithoautotroph*
- Energy from inorganic chemicals and carbon from organic carbon: *lithoheterotroph*
- Energy from organic carbon and carbon from organic carbon: *heterotroph*

Microbial metabolic pathways that use sulfur occupy all of the foregoing niches with the exception of the heterotroph, but there are sulfur-utilizing microbes that have the ability to shift to a hetrotophic metabolism if conditions require it and otherwise allow it. For example, some chemolithoautrophic thermophilic organisms can also function as opportunistic heterotrophs, being able to use organic as well as inorganic materials for energy production and cell growth (Stetter, 2006).

Microbial life has been found to be extremely robust and capable of surviving in a wide range of environmental conditions. As microbiologists have discovered species in diverse environments, the potential that microbial life may have evolved or may exist in other locations in the solar system has become a practical possibility. Aside from the chemical environment, which is a thread throughout this discussion, the physical environment can vary with regard to pressure and temperature. Temperature has by far the greatest effect on the bulk biochemistry of a microbe and provides the most evident limits to a viable environmental envelope. Microbial life can be divided into four temperature ranges:

1. *Hyperthermophiles:* with a temperature optimum greater than 80°C
2. *Thermophiles:* between 45 and 80°C
3. *Mesophiles:* between 15 and 45°C
4. *Psychrophiles:* less than 15°C

The current upper temperature limit for microbial life so far detected is 122°C (Takai et al., 2008).

Pressure is manifest at the high end by hydrostatic conditions and at the low end by conditions in the upper atmosphere. Microbes occupy the deepest depths of the ocean; in addition, they have been found as deep as 2 km in terrestrial subsurface environments and as high as 77 km in the atmosphere (Whitman, 2009).

Major oxidation–reduction pathways for microbes include:

- Aerobic oxygen utilization
- Nitrogen
- Iron
- Sulfur
- Hydrogen
- Methanogenesis

There are other comparatively minor pathways that involve other potentially labile transition metals or metalloids, and there are many subsets of oxidizing and reducing reactions involving nitrogen, iron, and sulfur chemistry. The process responsible for acid mine drainage, sulfide oxidation in the form of iron sulfides such as pyrite, is an example of redox pathways in the sulfur and iron system.

Sulfur is an extremely important inorganic energy source for microorganisms and can yield up to eight electrons in a stepwise fashion from sulfide (2−) to sulfate (6+). The oxidation of iron sulfide associated with anthropogenic acid mine drainage (AMD) or natural acid rock drainage (ARD) is extremely complex; it can, however, be summarized by two reactions:

$$FeS_2 + 3\tfrac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4{}^{2-}[6pt] \tag{7.1}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 16H^+ + 2SO_4{}^{2-} \tag{7.2}$$

It is important to note that this oxidation process does not oxidize iron. The iron in pyrite is ferrous in the mineral and remains ferrous when released into solution (Rimstidt and Vaughn, 2003). All of the oxidation involves sulfur; the energy that is exploited by microbial metabolism associated with AMD is based on the transfer of electrons from the sulfur in the pyrite. This also yields a wide variety of sulfur-based reaction products, which can in turn participate in additional processes (Douglas, 2005). In contrast, iron is also extremely bioreactive, but iron redox reactions involve only one electron: either ferric iron acting as an electron acceptor and reducing to ferrous iron, or ferrous iron acting as an electron donor and oxidizing to ferric iron. Rather than as a pure source of energy, iron serves to provide ready phase changes (from a dissolved species as ferrous iron to a precipitated species as pyrite) and as an active agent in redox processes, or, more accurately, as an electron shuttle.

The appearance of sulfate-reducing bacteria that use carbon to generate sulfide appears to be nearly simultaneous with the appearance of the anoxygenic photosynthetic production of sulfate approximately 3.5 billion years ago (Canfield and Raiswell, 1999). The isotopic nature of sulfide oxidation makes it difficult to identify specific processes in the deep geological record; however, recent published research indicates that sulfide oxidation was taking place approximately 3.4 billion years ago (Wacey et al., 2011). The evidence is the physical presence of pits and channels on the surface of pyrite grains, which are diagnostic of microbial processing in modern environments; of carbonaceous coatings on the grains, diagnostic of microbial life; and of nanograined layers of iron oxides, which are also a signature of biological processing. Microbial-driven sulfur species disproportionation reactions may also have evolved in a similar time frame (Philippot et al., 2007). Disproportionation reactions in the sulfur system are in essence self-referencing. Sulfur has a range of oxidation states from 2− to 6+. Disproportionation uses intermediate oxidation states of sulfur (elemental sulfur, sulfite, and thiosulfate) to generate both oxidized (sulfate with a 6+ charge) and reduced (hydrogen sulfide with a 2− charge) end members.

One way of understanding these microbial oxidation–reduction metabolic pathways is to think of them in terms of electron donors and electron acceptors. For example, in the case of sulfate reduction, in the presence of a source of carbon, electrons are removed from the carbon (the electron donor) and transferred to the sulfate (the electron acceptor). The carbon is oxidized (through repeated steps ultimately to carbon dioxide) and the sulfate is reduced to hydrogen sulfide.

Given robust environmental and chemical adaptability, microbial life in aggregate represents a significant portion of current biological activity on Earth. It is estimated that microbial life represents approximately 350 to 550 tons of cellular carbon on Earth; this is equal to 60 to 100% of the cellular carbon that can be attributed to plants (Keller and Hettich, 2009). In the case of the early Earth, very early metabolic pathways could have involved the cycling of hydrogen and ferrous iron, driven primarily by anoxygenic prototrophs (Canfield et al., 2006). Those marine rates of primary organic carbon production under early anaerobic conditions were an order of magnitude less than those observed in the current aerobic ecosystem (Canfield et al., 2006). However, this level of activity was enough to support a self-sustaining microbial ecosystem.

Further indication of the robust nature of living processes beyond metabolic processes is the recent discovery that microbes can substitute arsenic for phosphate in proteins and nucleic acids (Wolfe-Simon et al., 2010), demonstrating adaptability in fundamental biogeochemical structure and reproductive processes. This is a much more fundamental level of adaptability, beyond compensation for environmental conditions or utilizing diverse energy-tapping metabolic chemical pathways. This level of adaptability in particular reflects on the potential for life being present at other locations in the solar system.

Review of the Chemistry of Acid Mine Drainage

Placing the effects of sulfide oxidation into the overall metabolic cycling of sulfur, the evolutionary development of sulfur-processing microbes, and the potential role of sulfide oxidation in extraterrestrial life processes bears some consideration here, as it is worthwhile to provide a brief background on acid mine drainage in order to place the process into the context of this discussion. At the core of acid mine drainage is the oxidation of iron sulfides. For the purpose of this discussion, the primary focus will be on pyrite.

Aside from oxidation reactions, it is important with regard to overall geochemical conditions that may have had an effect on the origin of life to understand that pyrite represents a deep thermodynamic sink for anaerobic reducing conditions. It is the most stable iron mineral under anaerobic conditions, and it has considerable reducing power to drive chemical reactions on its surface (Blochl et al., 1992). Under the proper geochemical conditions, pyrite can reduce protons to molecular hydrogen (H_2) and nitrate to ammonia, and drive other multiple reductive organic reactions.

The oxidation of pyrite is not a simple process. Oxidation can take place by abiotic and biological processes over a wide range of environmental conditions. In general, microbial activity may account for approximately 70% of the pyrite dissolution seen at acid mine drainage sites (Newman and Banfield, 2002). The following reactions offer a simplified view of key steps in the process:

(7.3)

Then further acidification takes place by the oxidation of iron:

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+ \quad (7.4)$$

Ferric iron is an oxidant of pyrite under strongly acidic conditions:

$$FeS_2 + \tfrac{15}{4}O_2 + \tfrac{7}{2}H_2O \rightarrow Fe(OH)_{3(S)} + 2SO_4{}^{2-} + 4H^+ \quad (7.5)$$

In addition, it is important to point out the critical role that microbial processing plays in the oxidation of pyrite. The rate-limiting step in the oxidation of pyrite and the formation of acid mine drainage is the oxidation of ferrous iron (Singer and Stumm, 1970) that is produced in reactions (7.3) and (7.4). Under acidic conditions the half-life of ferrous iron undergoing abiotic oxidation by oxygen is in the range of 1000 days. Microbial processes accelerate the oxidation rate of ferrous iron by over a million-fold, which is a profound contribution to the process. The microbial enhancement of ferrous iron oxidation under acid conditions by six orders of magnitude compared to abiotic processes is particularly significant since the ferric iron reaction product produced biologically further enhances the pyrite dissolution process (McGuire et al., 2001). To take place, this all requires the presence of oxygen, of course.

The abiotic oxidation of pyrite by oxygen is to some degree also governed by the availability of reactive sites on the mineral surface along with the presence of both oxygen and water. Ferric iron is formed, and that in turn facilitates the dissociation of water (Guevremont et al., 1998). The most studied organism that can drive this process is *Acidithiobacillus ferrooxidans*. This organism is moderately thermophilic; it is an obligate autotroph and fixes carbon from the atmosphere; it can fix atmospheric nitrogen; it has flexible energy pathways that can oxidize ferrous iron to ferric iron or sulfide to acidic sulfate; it has an optimum pH range of 1.5 to 2.5; and although it is preferentially an aerobe, it can use sulfide as an electron donor and ferric iron as an electron acceptor under anaerobic conditions. It has a robust and flexible metabolism and appears to be ubiquitous in the environment (Rawlings and Kusano, 1994). Given that demonstrated flexibility, it should receive some consideration as being a component in extreme environments such as those represented potentially by extraterrestrial conditions.

In detail, research indicates that the actual oxidation process for pyrite is extremely complex. The complete oxidation and dissolution of pyrite to ferrous iron and sulfate entail the total transfer of seven electrons, typically one or two at a time. In addition, the surface of the pyrite exhibits electroactivity as well, with localized anodic reaction sites associated with the sulfur and cathodic reaction sites associated with the iron, with the rate-determining step determined by the iron reaction (Rimstidt and Vaughan, 2003). The potential accumulation of reaction products on the surface of the pyrite provides an additional complication (Pisapia et al., 2007). The accumulation of elemental sulfur demonstrates passivation effects, but the presence of iron-oxidizing bacteria produces ferric iron, which in turn can oxidize the elemental sulfur to sulfate, removing it from the pyrite surface (Drushel et al., 2004). The ferric iron that is formed also facilities the dissociation of water (Guevremont et al., 1998).

The abiotic oxidation of pyrite by oxygen is to some degree governed by the availability of reactive sites on the mineral surface along with the presence of both oxygen and water. This means that the pyrite oxidation process is also dependent on grain size, crystalline versus amorphous structure, crystal defects, and impurities present in the pyrite. In addition to oxidation in the presence of oxygen, iron sulfides can be oxidized in anoxic sediments by reactions with manganese oxide (MnO_2) or nitrate. This implies that simple burial of iron sulfides may not ensure their chemical stability (Schippers and Jorgensen, 2001).

The Origin and Evolution of Life on Earth

Important Background Details

The manipulation of energy flow in chemical processes is at the core of the vitality of life. To properly understand the role of energy in the origin of life, it is important to be knowledgeable about a few more details regarding energy. Five fundamental forms of energy have a potential impact on microbes.

1. *Physical energy:* $E = \frac{1}{2}mv^2$, where E is energy, m is mass, and v is velocity. Physical energy is not utilized directly by microbial organisms. However, during the time of the early Earth, repeated and intense bombardment took place. That physical energy caused physical disruption and contributed other forms of energy (such as thermal energy) that did have an effect on early forms of life. In the case of the potential for life on satellites around Jupiter or Saturn, physical energy in the form of tides converted to thermal energy is potentially a critical contribution.
2. *Electromagnetic energy:* $E = h\nu$, where E is energy, h is Planck's constant, and ν is the frequency of the radiation. The most obvious impact of electromagnetic energy is oxygenic photosynthesis. However, there are also anoxygenic photosynthetic pathways involving iron and sulfur among other elements that probably had a significant influence with regard to the early development of life. In the upper atmosphere of the Earth and the surfaces of planetary satellites, electromagnetic energy flux can be intense and include the effects of ionizing radiation, causing radiolysis, which will drive abiotic reaction processes.
3. *Chemical energy:* $\Delta G = \Delta H - T\,\Delta S$, where G is the Gibbs free energy, H the enthalpy, T the absolute temperature, and S the entropy. This characterizes the two primary forces associated with chemical reactions: the drive toward stable chemical bonding, represented by ΔH, and the effects of driving to states of higher disorder, represented by ΔS.

   Reactions that are exergonic (exothermic) have a negative ΔG value and tend to drive forward independently. The products of the reactions have less free energy than the feedstocks to the reaction, which difference (a negative ΔG) is released to the environment or is available for other processes, such as metabolism. Aside from oxygenic photosynthesis chemical energy in its many forms is a core form of energy manipulation by life.

   Finally, with regards to AMD or ARD, the oxidation of pyrite is extremely energetic:

   $$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+$$

   with a $\Delta G^{(0)}$ value of −749.5 kJ/mol (Schafer et al., 1999).
4. *Electric energy:* $E = UIt$, where E is the energy, U the voltage, I the current (amperage), and t the time. There are microbial systems that do utilize electrical energy by methods that include extracellular conduits; they are responsible for the phenomena represented by microbial fuel cells.
5. *Thermal energy*, which is proportional to temperature, is not used directly by organisms to support metabolic processes; it can, however, affect reaction rates and the physical properties of the cell wall and cellular contents.

There is another type of fundamental energy that is not included in the list above: *nuclear energy* (beyond the radiolysis effects of ionizing radiation noted above). No known organism utilizes nuclear energy directly. However, it does have a profound indirect impact in the form of heat and light from nuclear fusion in the Sun and geothermal heat from nuclear fission in the crust, mantle, and core of the Earth.

It is also important to have an appreciation of the magnitude of the development of life on geological history. First the current atmosphere of the Earth is a completely biogenic product with the dominance of oxygen, due to the evolution of oxygenic photosynthesis in conjunction with other biogeochemical crustal processing that provided additional gas balance controls. The composition of the continental crust is a product of biological processing over the last 3.8 billion years of Earth's history. Weathering of rocks exposed on Earth's surface is a process that has been enhanced biologically since the very early Precambrian. Iron, in particular, is an important part of this process. The iron that originates from iron-reduced rocks originating from the mantel is first oxidized; this includes basalts in oceanic spreading centers. Surface weathering removes the iron and delivers silica-rich detrital material to ocean basins, forming shales, which, in turn, are subducted to form iron-poor oxidized granites. Carbon-rich black shale provides an even stronger biological signature. Those black shales and their metamorphosed equivalents are enriched in uranium, which results in preferential heating that ultimately provides weak points in crustal rocks that serve as epicenters for continental crustal tectonics such as thrust faulting (Sleep and Bird, 2008).

The Origin of Life

In the literature there is a great deal of discussion of the *last universal common ancestor* (LUCA), the organism from which all subsequent life evolved. Because only a small subset of bacteria are cable of photosynthesis, it is probable that LUCA predated photosynthetic microbes. There are two dominant theories with regard to the environment associated with the origin of that organism: heterotrophic theory and autotrophic theory (Wachtershauser, 1990, 1994). In *heterotrophic theory*, life began in a soup of chemicals that included amino acids and other key chemicals, and the energy production process involved the fermentation of simple organic chemicals available in the environment.

In *autotrophic theory*, initial processes involve low-molecular-mass simple compounds with no preexisting building blocks present. Energy is derived from the available free energy of inorganic compounds that are in the environment but in nonequilibrium conditions. Nonequilibrium conditions mean that there are concentration gradients between reactive inorganic compounds and their reaction products and potentially differences in the physical environment as well, such as temperature gradients. Geothermal systems represent a common example of conditions that support autotrophic processes.

Conditions on the Early Earth

To understand how early life may have originated and the environmental conditions under which that process took place, it is first important to review what conditions were like on the early Earth. For purposes of this discussion, the Hadean dates from 4.5 to 3.8 billion years ago, and the Archaea dates from 3.8 to 2.5 billion years ago. There is almost no geological record from the Hadean, and the record from the Archaea is minimal. The Hadean was a time representative of initial crust formation and there is some evidence which suggests that liquid water existed on Earth's surface as early as 4.4 billion years ago (Lunine, 2006). However, the geological record indicates that from the period of 4.55 billion years ago to approximately 4.2 billion years ago, the Earth was subject to repeated impacts of ocean-boiling intensity; those were sterilizing events. In addition, the presence of liquid water does not greatly limit surface temperatures. With an abundant supply (similar to current Earth conditions), liquid water can exist up to its critical point at 374°C (705°F) (Kasting and Ono, 2006). The physical process is similar to that in a pressure cooker, where increasing confinement pressures prevent temperature increases from causing water to boil. In the early Archaea, surface temperatures may have been as high as 70°C, one condition that may be responsible for evidence which indicates that the first forms of relatively abundant microbial

life to appear were thermophiles.

As time progressed, conditions did change. With regard to general temperature profiles over long geological time frames, there is evidence for periods of continental glaciation, but isotopic data indicate that average temperatures declined from near 80°C at the end of the Hadean, to approximately 70°C by the end of the Archaea, to 25 to 30°C by the end of the Precambrian (Gaucher et al., 2010). The surface and crust of modern Earth is to a large part the result of biogenic processing over this time frame. During the geological evolution of Earth over billions of years there has been a continuous release of carbon dioxide, largely from the mantle. In turn, this carbon dioxide has been reduced (forming organic matter) by the activity of photoautotrophic organisms. Further carbon-reducing processes have released inorganic species that have oxidizing power. Ferric iron has been dominant at an estimated 73% of the oxidizing equivalents produced beginning 3.8 billion years ago; sulfate represents 26% and oxygen only 3% (Hayes and Waldbauer, 2006). The consequences of this redox processing are important to bear in mind regarding the origin of life. Over geological time, minerals common to the surface of the Earth have evolved with time as well. Approximately two-thirds of all known mineral species are weathered products interacting with Earth's oxygen-rich atmosphere. The abundance and form of minerals under reducing conditions that were distinctly different than current conditions and that were present for the bulk of the geological history of Earth must be taken into account for early origin-of-life scenarios that call on chemical–mineral interactions.

What We Know of Early Life

Understanding what took place during the very early development of life is a very difficult process. The farther back in time we go, the higher the degree of geological processing that has taken place. The organisms themselves do not have the character (hard parts) that allows for the direct formation of fossils. The predominance of usable evidence involves by-products of metabolic processing of the inorganic chemicals that lie at the core of electron acceptor and donor reactions. This typically requires the formation of a solid precipitated phase that can be preserved. The use of isotopic studies is extremely helpful, but once again, large pieces of the process may be missing. Sulfur, in particular, is distinctly fractionated by biological activity and represents the chemical most likely to aid in the detection of biological activity. Flores (2006) has evaluated Europa's icy and patchy surfaces. Isotopic evaluations of other chemical participants, such as carbon and oxygen, can be helpful as well. But affecting the forensics of the sulfur cycle is the fact that while solid metal sulfides can be preserved, the soluble reaction products are not typically preserved. An acid mine drainage sulfide oxidation system is an example of an entity in which soluble products are generated and not preserved.

The development of tools to allow for detailed genetic analysis such as rRNA sequencing of organisms generated the hope that it would prove to be a valuable tool for evaluation of the origin and evolution of life. Genetic analysis has made significant contributions; for example, the realization that the Archaea represented a third and distinct kingdom of life came about through the use of genetic evaluations. Although rRNA sequencing is a powerful tool, it cannot be used reliably to extract the timing of the events typically shown in what are termed *phylogenetic trees*. It can, however, serve to evaluate the sequence of genetic changes (Pace, 1997). This is complicated further by the recognition that lateral transfer of DNA among microorganisms has been a significant process in the past (Doolittle and Papke, 2006) and the present. Based on the current level of knowledge, as genetic analysis has been performed on increasing numbers of microbial populations exhibiting diverse metabolic capacities, it has become clear that horizontal gene transfer has been an extremely common process, making the identification of an original ancestor by phylogenic analysis extremely unlikely. The level of uncertainty this generates is significant;

for example, Cavalier-Smith (2006) postulates that the archaea are a relatively recent (0.9 billion years ago) development, with archaean methanogenesis younger yet, at 0.7 billon years. This would make the archaeal domain the most recent and almost contemporaneous with the appearance of the multicellular life that was possible with the presence of high concentrations of oxygen in the atmosphere.

The evidence for very high levels of lateral gene transfer indicates that microbial life has an extremely high level of flexibility and adaptability. It is not uncommon for microorganisms to possess the capacity to exploit a wide range of electron acceptors under a wide range of redox conditions. The term *facultative* is often applied to these organisms. Singer et al. (2011) have recently published a review of an adaptive marine organism and have proposed a term for microbes of this type that is precisely descriptive: *opportunitroph*.

Although in many instances not discernibly metabolically active, viable microorganisms with widely diverse, preferential metabolic habitats can be found in almost any environment. The potential for the indigenous exploitation of biogeochemical energy gradients of any type is a ubiquitous condition on Earth (Falowski et al., 2008).

During the Hadean bombardment it is likely that multiple asteroid impacts of a size sufficient to boil the oceans took place (a 300-km asteroid will boil part of the ocean, asteroids greater than 400 to 500 km will boil the entire ocean) multiple times (Sleep, 2010). After such a strike it would take a few thousand years for surface conditions to return to normal. In that environment it is possible that microorganisms could have survived in the subsurface at depths of approximately 1 km. This would have required regions where the geothermal gradients were low enough to allow for acceptable temperatures at that depth. It is also possible that life may have originated several times and was subsequently wiped out totally: that what we observe today came out of the latter stages of an extremely violent and destructive birth.

Given those limitations, we may not have knowledge of the first ancestor, but there are things that we do know:

- On the early Earth, evidence indicates that by 3.8 billion years ago anoxygenic photosynthesis was a dominant metabolic pathway, principally sulfate based in the oceans and iron based on land (Sleep et al., 2008).
- However, it is most likely that the first life was chemoautotrophic rather than photoautotrophic (Gaucher et al., 2010).
- By approximately 3.5 billion years ago, sulfate-reducing organisms had evolved and were active (Shen et al., 2009).
- There is physical evidence that biologically driven sulfide oxidation was taking place 3.4 billion years ago (Wacey et al., 2011)
- Isotopic data indicate that methanogenesis was present by approximately 3.5 billion years ago as well.
- It is striking that oxygen photosynthesis is the most complex energy management process found in nature. It requires over 100 genes to drive the chemistry. Despite this, evidence indicates that this process had evolved and was active approximately 3 billion years ago (Falkowski et al., 2008).

The picture that emerges is that upon cessation of the extremely turbulent Hadean period, life rapidly appeared with microbial complexity fully equal to that we see in the present. The ultimate appearance of multicellular organisms at the end of the Precambrian approximately 600 million years ago was a function of the availability of oxygen, which allowed for highly efficient energy generation via effective transport

processes that allowed a collection of cells (rather than isolated cells) to function. The basic metabolic pathways were, however, present over 3 billion years ago.

The result of the uncertainty regarding hard facts and evidence that can be found concerning the origin of life has led to speculation about how life originated. These scenarios are based on sound scientific principles and knowledge. But it must be borne in mind that these are possibilities, not fact. One of the reasons (among many) that the search for extraterrestrial life is so important is that the observation of life in that setting could contribute significantly to our understanding of the origin of life on Earth as well.

There are several key elements in any origin-of-life scenario, one, of course, being energy. As described earlier, energy in many forms was readily available on the early Earth, and that aspect of the origin question is well understood. A second issue is structural. For a processing system to be termed *living*, it must have some form of literal physical organization that allows it to contain and control key biogeochemical processes, isolated from the external environment to some degree. Finally, and most important, and most problematic with regard to origins, life must have a way to replicate and to do so in a manner that preserves its key life-defining and life-supporting character.

Regarding the consideration of structural needs, microbes are chemical-processing machines that are able to function because processing and other essential metabolic needs are enclosed within a discrete structural envelope. Modern cells have isolating walls that are composed of complex mixtures of lipids, proteins, and carbohydrates. The presence of a cell wall is an essential component of animate matter. This allows a microorganism to have an available microspace that protects nucleic acids, provides mechanical stability, and allows the creation and maintenance of a controlled biochemical environment (Spitzer and Poolman, 2009). It is also important that the cell wall have controlled permeability that allows communication with the physical–chemical environment outside the cell.

There are examples of very early possible enhancements of structural integrity that do not include encapsulation. Work has been done to evaluate the possibility that crystalline surfaces of minerals may have had a role in the origin of life. This includes facilitation of self-organizing condensation polymerization reactions on the surfaces of clays; the concentration of other organic compounds, such as sugars and amino acids by silicates, carbonates, and oxides; and direct stimulation of organic chemical reactions by transition metal sulfides and oxides (Hazen and Sverjensky, 2010). It is possible that catalytic reactions at organophilic silica mineral surfaces of zeolites or feldspars supported the ability to generate replicating biopolymers (Smith et al., 1999). Evaporation may also play an important contributory role in the formation of polymers on mineral surfaces. That, however, calls for an environment in which evaporation can take place. That, in turn, means that having a large proximal moon that generates tides physically may be a significant factor associated with the origin of life.

Further speculation has taken place with regard to transition into the full encapsulation of the cell. Examples include:

- The conversion of fatty acid micelles into vesicles stimulated by montmorillonite (Hanczyc et al., 2003).
- Inside mica sheets (Hansma, 2008).
- Iron monosulfide precipitation cells (Russell and Hall, 1997; Martin and Russell, 2003).
- Porosity adjacent to thermal flow systems can have environments of the type envisioned for emergent life. Thermal and chemical diffusion can allow for the accumulation of chemical species in plugged pore spaces. In plugged fracture porosity, chemical species tend to collect and concentrate in the distal end of the pore space. Small aperture fractures tend to accumulate only long-chain polymers,

whereas wider-aperture fractures collect short- and long-chain polymers (Baaske et al., 2007). This system may have served as a semipermeable membrane for emergent life, providing a serviceable substitute for later semipermeable cell membranes constructed by the organism.

Finally, all these scenarios have a wide range of organizational stability, which is important to physically contain metabolic processes. However, it is becoming increasingly clear that the core issue for the origin of life is the capacity to replicate accurately, not the availability of metabolic processes able to perform energy extraction. Chemical modeling (Vasas et al., 2010) and evaluation of chemical reaction processes (Orgel, 2000) strongly indicate that a purely compositional energy-deriving system is unstable and cannot evolve in a manner that transmits inheritance information; a stable storage-based information transmission system is essential to sustain life that can evolve (Vasas et al., 2010).

Life in The Solar System

There are currently five candidates for locations at which life has originated or even still exists:

- Mars
- Europa, a Galilean moon of Jupiter; second outward from the innermost moon, Io
  - The surface of Europa is covered with a layer of water up to 100 km thick. Indirect evidence indicates that there is liquid water present beneath an icy surface crust. Hubble has detected evidence of geysers.
- Enceladus, one of Saturn's moons
  - Enceladus has been observed to have geysers of liquid water that contains hydrocarbons.
- Saturn's moon, Titan
  - There are indications that Titan also has a liquid ocean beneath its surface crust (Lorenz et al., 2008; Sotin and Tobie, 2008). This is supported by cosmochemical and thermal models as well as by detailed evaluation of its rotational period by Cassini radar observations.
- Castillo, which has liquid water covered by an icy crust

Mars, Europa, and Enceladus have had the greatest amount of information collected about them.

Mars

Mars is, and has historically been, a candidate for potentially bearing life. It is also the most highly assessed in that regard as well, with multiple probes of increasing sophistication having been placed in orbit and on the surface. Earlier in the chapter we focused on energy systems, structural cohesion, and the ability to replicate accurately as core requirements for life. What has been left unsaid in this discussion is the requirement for liquid water for all of these processes to take place. Life in any form that we know of absolutely requires the presence of liquid water to exist. In the case of Mars, much of the assessment that has proven most promising for the presence of life is concrete evidence for the existence of an abundance of water on the surface of Mars in its geological past. In addition, in contrast to Earth, due to the lack of extensive geological processing, direct evidence of processes associated with the origin of life may be better found on Mars (McKay, 2010).

There are geomorphological features on the surface of Mars that obviously represent a past in which flowing fluids were present. Specific mineralogical evidence has become available from successful

deployment of robotic instrumentation packages to the surface of Mars. The discovery of hydrated silicates (phyllosilicates) in the crust of Mars is one of the indications that in the deep past on Mars, liquid water was available on its surface (Carter et al., 2010). Magnesium carbonates for that era of Mars' history have also been found, additionally indicating an early atmosphere that was warmer, wetter, and richer in carbon dioxide (Morris et al., 2010). The detection of chlorides in the southern highlands of Mars does provide further evidence of water at the Martian surface (Osterloo et al., 2008). Sulfates have also been found on Mars' surface (Bibring et al., 2006).

The Mars Reconnaissance Orbiter High Resolution Imaging Science Experiment has found visual indications of flowing water on Mars that is currently taking place on a seasonal basis (McEwen et al., 2011). The observations are in a location where there is also geomorphological evidence of flow water. These are tentative results, but potentially important. It is also thought that the waters observed are brines, with an implication for the presence of potential energy yielding inorganic species such as sulfate.

Data gathered over recent years indicate that Mars has had a three-stage geological history: an early stage with surface water at neutral-pH conditions; a stage during which surface water became acidic; and a third (and longest and current) stage, during which there was no (or potentially little) surface water, and iron oxides underwent alteration. All three of these stages were complete by approximately 3.5 billion years ago. Only the first stage would have had conditions amenable to surface-based life as we know it.

Aside from the recent hints at seasonally based water flow, the exploration of Mars has also shown that there is a relative abundance of water in the form of ice at the north and south poles of Mars. Potential water volumes are great enough to cover Mars theoretically with a layer of water (if liquid) 20 m deep (Gurnett, 2009). Current near-surface conditions on Mars have proven inhospitable to life, with highly reactive and toxic peroxides found in surficial soils. However, the question remains if life could still be present in niches represented by shallow subsurface soils, beneath water-bearing permafrost, or in the polar ice caps.

The latter two environments (among other reasons) have stimulated research regarding the ability of microbial life on Earth to survive and even thrive in ice. It has been demonstrated that viable microbial activity takes place at temperatures near the freezing point of water or even significantly below (−40°C) that point (Price and Sowers, 2004). Survival within ice crystals has been observed supported by diffusion-controlled transport of biogenic gases (Rohde and Price, 2007). These represent low-temperature, diverse, complete, and viable ecological systems. Aerobic and anaerobic populations have been identified (Perreault et al., 2008), metabolic pathways include the processing of iron and sulfur compounds (Mikucki and Priscu, 2007), and there is increasing evidence that sulfur-based metabolic pathways are actually dominant (Sattley and Madigan, 2006; Perreault et al., 2007).

In the case of Mars, methane is present in its atmosphere at low concentrations. Methane is a reactive species in an atmosphere and it is further estimated that the existing concentrations of methane in the atmosphere of Mars would be destroyed by ultraviolet photolysis in approximately 340 years. To produce methane continually via abiotic means at the concentration observed would require active magmatism and hydrothermal alteration by water that contains carbon dioxide. Based on current observations, that type of geological activity is not present on Mars to the degree required to produce the concentrations of methane observed. An alternative would be the microbial production of methane from microorganisms that are present in appropriate environments on Mars. Based on the ice caps alone, the estimates of the potential for microbial activity based on those observed in ice on Earth fall well within the range of those required to produce the methane observed in the Martian atmosphere (Tung et al., 2005). An opportunity to perform an isotopic evaluation of that methane would be one means of confirming a biological versus an abiotic origin.

If life originated on Mars, it probably did so during the historical stage at which liquid water was readily available at the surface. If life continues to exist on Mars, it is present in ecological niches associated with the ice caps, and it is likely to be a surviving residue, not a dynamic and robust planetwide population.

Europa

The surface of Europa is unique in that it is not heavily cratered. That means that in a geological sense that surface is relatively fresh, indicating the effects of active transference of material from the interior of Europa to the exterior. That material is dominantly water, and the geological drivers for the process are tidal forces associated with Jupiter. The energy associated with tidal forces driven by near orbit around Jupiter is significant. For an obvious example, the heat generated from tidal forces exerted by Jupiter on nearby Io is sufficient to melt sulfur and generate the sulfur volcanoes observed. This represents a heat flow that is 30 times that of the mean heat flow from Earth's midoceanic ridges. There is no water on Io, but the availability of significant heat is a critical element for the existence of life, and that type of mechanically generated heat is also present on nearby Europa. Models have also indicated that there is sufficient geothermal and tidal heating to keep the ocean in a liquid state beneath its outer layer of ice (Chyba and Phillips, 2002). With a depth of 100 km, Europa's ocean would represent twice the volume of water in Earth's oceans.

There are multiple lines of evidence which indicate that Europa has an ocean beneath its surface crust. This includes assessment of Europa's magnetic field by the *Galileo* spacecraft (Kivelson et al., 2000). The surficial icy crust of Europa is estimated to be 10 to 100 km thick, which prevents directly any potential metabolic energy pathway that relies on exposure to light. Chemolithotrophic metabolism is possible, driven by potential hydrothermal systems in the rocks that underlie the ocean.

Oxidants are created on the surface by interaction of the water in ice with ultraviolet radiation (photolysis) and the particles in Jupiter's magnetosphere (radiolysis). This produces hydrogen, oxygen, hydrogen peroxide, hydroxide radicals, and other oxidized inorganic species in the shallow ice. There is a faint but observable oxygen atmosphere associated with Europa that is produced by those processes. Tied in with ice convection of other reactive species on the surface crust, the end result is a net energy flux into Europa's ocean. However, it is at a rate that is three orders of magnitude less than those currently observed in the oceans of Earth.

Sulfur has been observed on the surface of Europa; it is seen in patches on top of the surficial ice (Chela-Flores, 2006). This suggests that this sulfur originates from geological processing of the core and lithic crust internal to Europa. A potential alternative source of the sulfur is Io, a nearby Galilean moon with sulfur-based volcanism. However, sulfur from Io or from the general Jovian inner system environment would deposit as uniform layers rather than the patches observed.

Where deep ocean hydrothermal systems and their associated biota have been examined on Earth, more than 99% of the available chemical energy comes from sulfate reduction, sulfur oxidation, and other anaerobic metabolic pathways (Gaidos et al., 1999). However, without a flux of oxidants from the surface (sulfate, oxygen, and carbon dioxide), only the reduction of elemental sulfur and methanogenesis would be available as energy sources. In the case of Europa, surface turnover and transport of oxidants into the underlying ocean would require the solid-state convection of surficial ice. The surface of Europa shows evidence of healing by such convection processes, and it is estimated that the current surface is somewhere between 10 and 100 million years old.

There may also be potential for life-supporting conditions driven solely by internal geochemical

dynamics, without the need for cycling of the crustal surface. Europa appears to have a metal core and a silicate mantle in association with a heat flux from the core that is 10 to 30% of that observed on Earth. Those similar conditions appear to have driven significant volcanic activity on Mars and may be sufficient to drive geothermal systems on Europa as well. On Earth, the mantle and crust have become oxidized over geological time. This results in carbon being emitted from contacting geothermal waters in the form of carbon dioxide. Geological conditions on Europa would be more reducing if the availability of oxidants from the surface is limited, as in that condition, carbon would outgas as methane. Similarly, sulfur in the interior would appear as sulfide rather than as sulfur or sulfate. Overall, sulfate reduction would not be a sustainable process. What would remain would be processes that include the use of oxidized metals such as ferric iron. Iron-reducing bacteria are common on Earth, as are hydrogen-, methane-, and sulfur/sulfide-oxidizing species.

At a low level of activity, life could exist driven by the reduction of elemental sulfur and methanogenesis, with sulfur, carbon, iron, and hydrogen provided by the geothermal system and chemical processes aided by the effects of temperature differentials on reaction kinetics and reaction equilibria. With regard to assessment for life, indications of chemical disequilibrium in the oceans of Europa would not be a direct sign of life; that would only indicate the availability of viable energy pathways to support life. However, evidence of the equilibration of sulfur and carbon species by redox reactions at low temperatures would be an indication for the presence of life (Zolotov and Shock, 2004).

Enceladus

One of the unexpected results from the *Cassini* probe sent to Saturn was the observation of fountain-like discharges from its surface. A significant effort has been spent to characterize those features further. The plumes that discharge from Enceladus contain water, methane, carbon dioxide, and nitrogen. The plumes are emitted from a tectonically active and thermally warm area on the south pole. The 10 : 1 ratio of water vapor to other noncondensable phases (such as methane) is very close to those observed in terrestrial clathrates (in the range 6 : 1 to 8 : 1). The transport of heat, water, and other gases in association with clathrate decomposition represents large-scale convection systems beneath the surface of Enceladus (Kieffer et al., 2006). The plumes emitted are leaks from this convection system. These water-based geysers may be a result of the interaction of heat from depth with near-surface clathrates (Gioia et al., 2007).

Further assessment of the composition of the plumes emanating from Enceladus shows that the plume chemistry includes sodium chloride, sodium carbonate, and potassium. The water vapor and entrained inorganics are found in Saturn's E ring. In fact, the water and inorganics in the E ring have been traced back to the Enceladus plumes, which further support the presence of water in the moon (Kerr, 2009).

Although the surface of Enceladus is water ice, it has an overall density that is 60% greater than that of water, so that in addition to having approximately 100 km or water ice and clathrate beneath its icy surface crust, that water ice and clathrate are underlain by a rocky core that can act as a source of inorganics that are critical to life as well (Kieffer and Jakosky, 2008). It is also important to note that this water ice–clathrate system is dominated by water that is the critical element for life as we know it. Finally, methane clathrates on Earth are known to support viable microbial populations (Lanoil et al., 2001; Reed et al., 2002).

Synthesis and Conclusions

The absolute core for the generation and propagation of microbial life includes the availability of genes to

provide accurate reproduction, biochemical catalyst to support cellular metabolic processes and energy capture, and an encapsulating membrane to produce a viable integrated whole organism (even of the simplest type). These three needs must be met in a nearly simultaneous manner, and they are almost certainly the most difficult problems with regard to the origin of cellular life. Encapsulation is a physical issue, and energy sources are intrinsic to redox reactions driven by chemistry that is potentially universally available given the proper baseline conditions. From the energy perspective, gradients in the environment external to the cell are essential. This includes gradients of temperature, total dissolved solids, and chemical conditions that provide chemical pathways that yield free energy. This need is met at locations other than Earth.

The existence of active geological processing is probably essential for the continual existence of life. Depending on the time frame for life to originate, it is possible that life could originate multiple times at multiple locations during the early stages of the development of the solar system and planetary bodies. The Hayden age of bombardment obviously generated dynamic physical and geochemical conditions universally at that time. Today, Earth, Io, Enceladus, and possible Titan are volcanically or cryovolcanically active (Spencer et al., 2009). This is demonstrated by their appearance. Figure 7.2 shows the crater-free surface of Europa with linear features due to geological activity, Figure 7.3 shows a detail of those features, and Figure 7.4 is a view of the south pole of Enceladus showing the active zone of geological processing and venting. The area with craters probably represents a surface that is billions of years old. Of interest is the presence (along the left limb) of another relatively young surface (with no craters) that also shows signs of geological processes. Figure 7.5 shows one of the active tectonic features on Enceladus in detail. For there to be a continued presence of life from the deep geological past to the present, an active geology is essential in order to participate in the production of the requisite geochemical disequilibrium that is at the core of microbial energy systems.

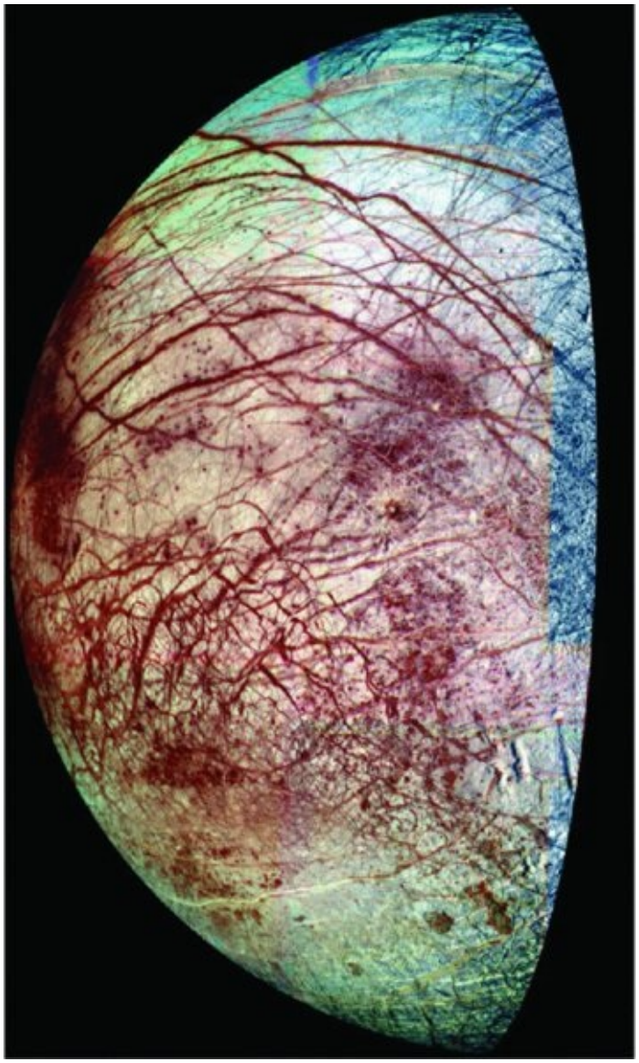


FIGURE 7.2 Crater-free surface of Europa. (Courtesy of NASA.)

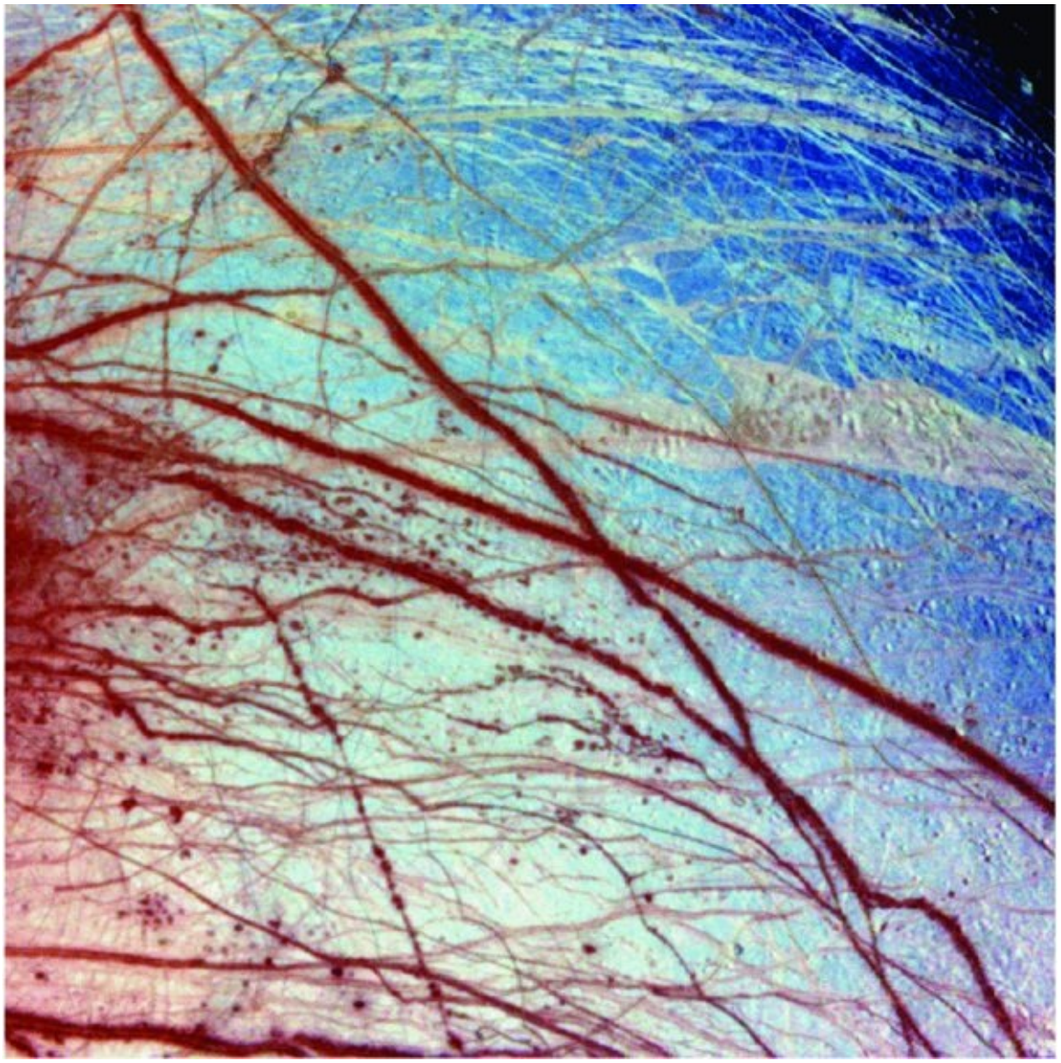


FIGURE 7.3 Detail of the surface of Europa. (Courtesy of NASA.)

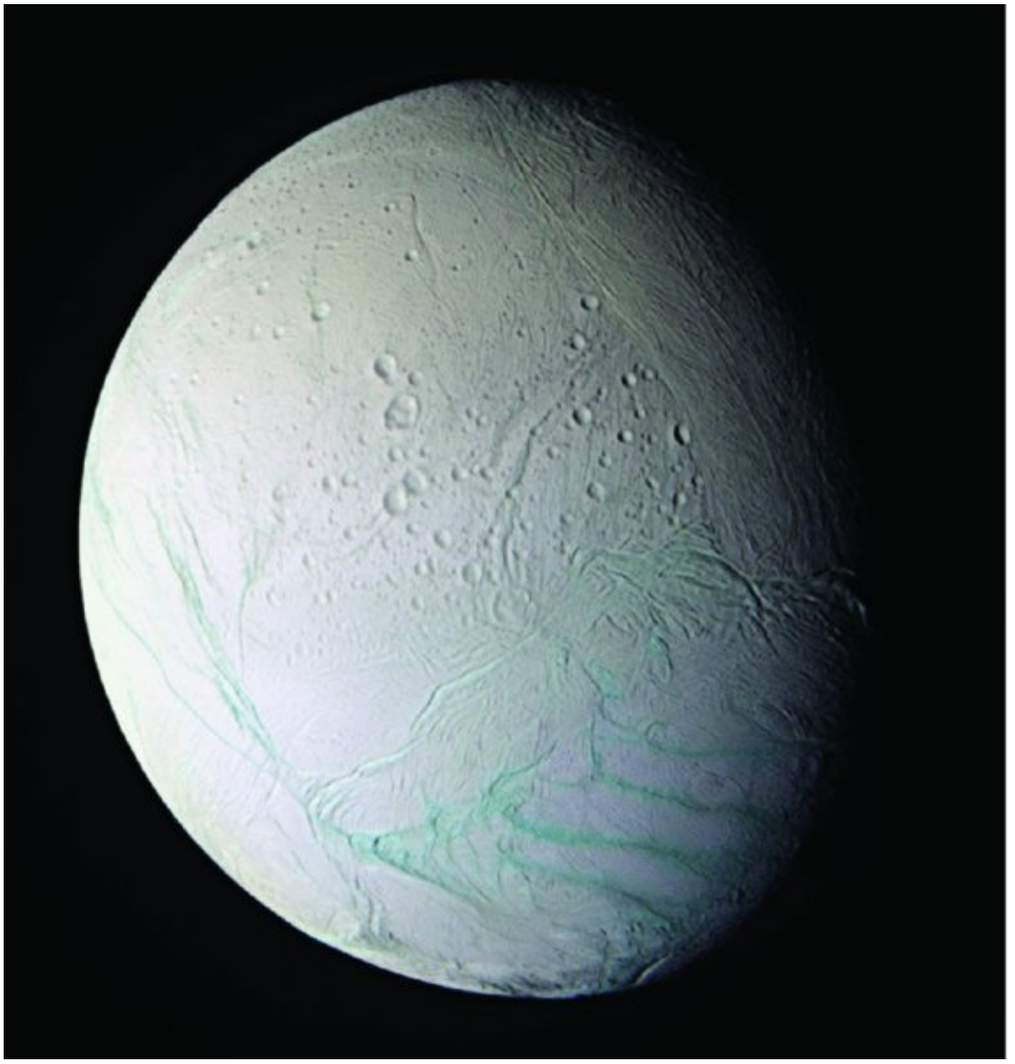


FIGURE 7.4 Crater-free surface of Enceladus. (Courtesy of NASA.)

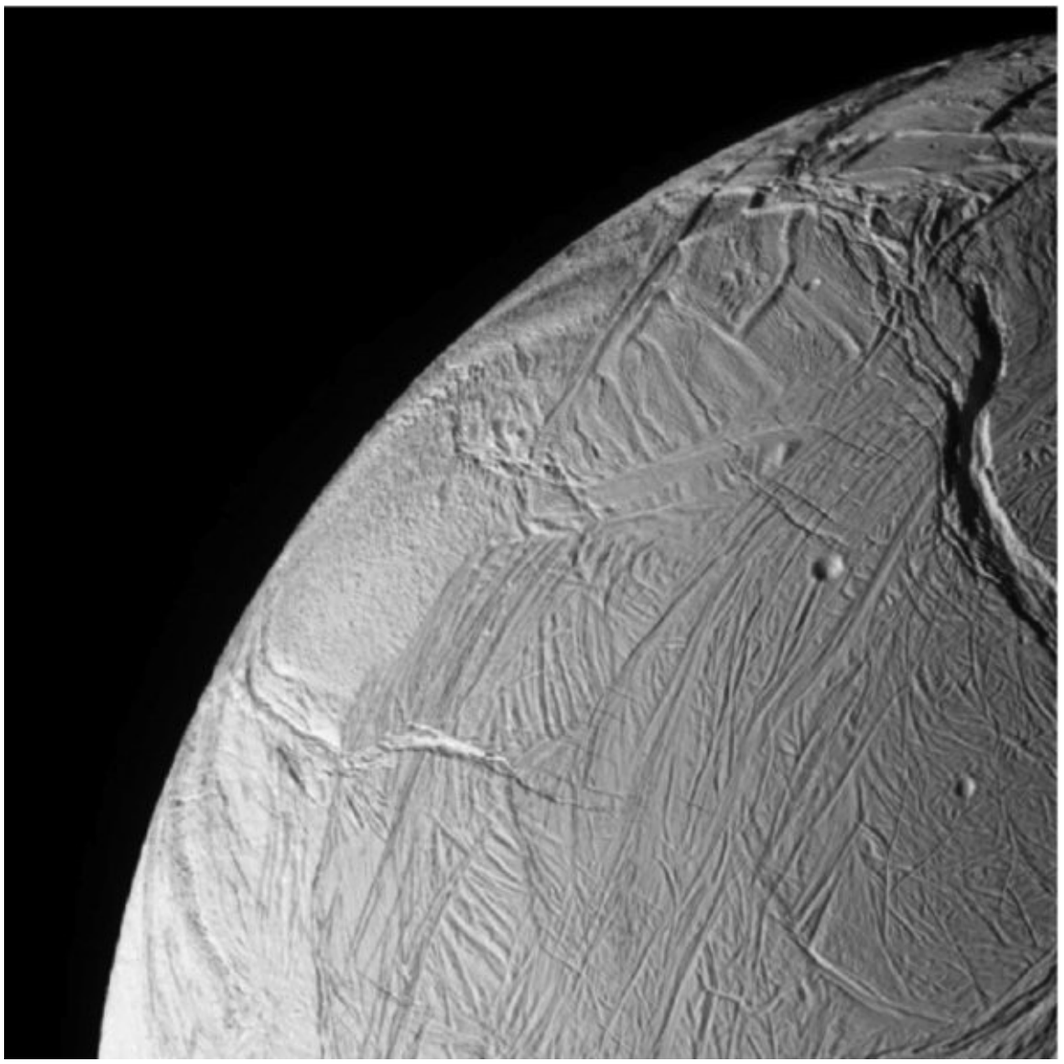


FIGURE 7.5 Detail of the surface of Enceladus. (Courtesy of NASA.)

Inherent in the long-term capacity to provide life-supporting energy from geological processing is the availability of potentially oxidizing species generated on the surface. In the case of the satellites in the orbit of giant gas planets such as Jupiter and Saturn, they are exposed to continuous magnetospheric plasma bombardment, which drives radiolysis of water, carbon, sulfur, and other chemical species that are on the surface of the satellite (Carlson et al., 1999; Teolis et al., 2010). This process creates oxidants such as oxygen. In turn, if geological tectonics is present, these oxidized species are brought into the interior, where water is present and chemical gradients can be generated between reduced and oxidized species. Those chemical gradients provide zones that are viable for supporting microbial life.

Although there is much speculation about the origin of life under high-temperature conditions, some of the specifics of the biochemistry of life argue against an initial origin at high temperatures. Rapid adaptation of early ancestors from an initial original ancestor to high temperatures exploiting physical and chemical gradients may be a more likely scenario. Several important biochemical systems demonstrate this (Bada and Lazcano, 2002). The nucleobases A, U, G, C, and T undergo rapid hydrolysis at temperatures above 0°C (Levy and Miller, 1998). The term *rapid* applies to geological time scales, but as an example, the decay half-life of cytosine at 0°C is 17,000 years. However, at elevated temperatures the half-lives of all the nucleobases decline to extremely low values, with ranges of 340 to 10,000 years at 25°C, 19 days to 1 year at 100°C, and 1 to 35 minutes at 250°C. Given those chemical constraints, the potential for the origination of life at locations such as Europa or Enceladus may actually be enhanced. What will be

limited is the overall magnitude of the microbial numbers that can be supported in the active but limited energy system.

The development of genetic reproduction systems is the one area that has the potential to be ultimately unique. That system on Earth is highly robust, as evidenced by the recent discovery that arsenic can be substituted for phosphorus in proteins and nucleotides (while maintaining the same basic chemical relationships). Competitive advantages are powerful components of successful evolution. The competitive advantage given to organisms by the development of oxygenic photosynthesis was orders of magnitude greater than that of competing processes. That development on a singular basis was so influential that photosynthesis evolved only once on Earth; no subsequent similar development has ever been able to compete successfully. The competitive advantage given by fundamental genetic capacity was even more profound.

The potential for the existence of life that supports physical systems for encapsulation, energy resources, and general environmental requirements does exist at other locations in the solar system. The discovery of extraterrestrial life in the solar system will be a significant event; whether that life has the same or a similar genetic structure or a completely different one will be the most important aspect of that event. Life on Mars with similar genetics may potentially be construed to be related to the development of life on Earth via transfer of material during the Hadean bombardment. The presence of life on giant gas satellites is much more likely to be a unique phenomenon, and all the more profound. Given the deep energy yield of sulfide oxidation, sulfur processing will be an important part of any biological systems that are found.

That brings us to a final word on pyrite oxidation and the microbial processes that drive AMD and ARD. The most common, or at least the most widely studied organism that is the cause is *Acidithiobacillus ferrooxidans*. With currently available technology and knowledge, we do not know if there was an example of *A. ferrooxidans* setting atop pyrite grains 3.4 billion years ago, leaching out those pits observed by Wacey et al. (2011). Little oxygen was present at that time, as evidenced partially by the presence of unaltered pyrite that could be populated by microbes. The source of the oxidizing power is unknown, with alternative electron acceptors such as sulfate, ferric iron, or nitrate being one set of biogenic pathways; and photolithography another, since the environment in which these materials are found is interpreted to have been shallow water. However, the details do not detract from the importance of sulfide oxidation as a microbial ecological niche over long geological time frames. Pyrite represents the deep end of the redox pool of minerals; as such, it is a profound energy source. That energy source was not and has not been ignored.

It appears that the oxidation of reduced sulfur compound is present in a diverse number of organisms, but the processing mechanism is common among them (Friedrich et al., 2001). An analogy is appropriate: Modern software is designed to run on enumerable hardware platforms that are evolving and increasingly diverse. Key algorithms for core functions and processes are expressed in the code and at some level are similar, if not identical, in all the hardware. The physical–chemical structure of microbes changes to accommodate extremes of temperature, salinity, pH, or other environmental conditions. Even in modern environments, researchers are finding that the geochemical setting is the dominant controller of microbial diversity (Mathur et al., 2007; Luo et al., 2009). However, core metabolic processes, including energy manipulation, are retained via the genetic code. So even though there was not an actual example of *A. ferrooxidans* attached to that pyrite and leaching pits in it 3.4 billion years ago, there are genes and subsequent enzymatic pathways that were there and have been active in the interval from then to the present, and present in a modern example of *A. ferrooxidans*. Parallel utilization of sulfur-based energy pools is likely to be found to be equally critical to any extraterrestrial life that is discovered in the future.

References and Suggested Reading

Baaske, P., Weinert, F.M., Duhr, S., Lemke, K.H., Russell, M.J., and Braun, D., 2007. Extreme accumulation of nucleotides in simulated hydrothermal pore systems. Proceedings of the National Academy of Sciences USA, vol. 104, no. 22, pp. 9346–9351.

Bada, J.L., and Lazcano, A., 2002. Some like it hot, but not the first biomolecules. Science, vol. 296, pp. 1982–1983.

Bibring, J.-P., Langevin, Y., Mustard, J.F., Poulet, F., Arvidson, R., Gendrin, A., Gondet, B., Mangold, N., Pinte, P., Forget, F., and the OMEGA Team, 2006. Global mineralogical and aqueous Mars history derived from OMEGA/Mars Express data. Science, vol. 312, pp. 400–404.

Blochl, E., Keller, M., Wachtershauser, G., and Stetter, K.O., 1992. Reactions depending on iron sulfide and liking geochemistry with biochemistry. Proceedings of the National Academy of Sciences USA, vol. 89, pp. 8117–8120.

Canfield, D.E., and Raiswell, R., 1999. The evolution of the sulfur cycle. American Journal of Science, vol. 299, pp. 697–723.

Canfield, D.E., Rosing, M.T., and Bjerrum, C., 2006. Early anaerobic metabolisms. Philosophical Transactions of the Royal Society B, vol. 361, pp. 1819–1836.

Carlson, R.W., Johnson, R.E., and Anderson, M.S., 1999. Sulfuric acid on Europa and the radiolytic sulfur-cycle. Science, vol. 286, no. 5437, pp. 97–99.

Carter, J., Poulet, F., Bibring, J.-P., and Murchie, S., 2010. Detection of hydrated silicates in crustal outcrops in the northern plains of Mars. Science, vol. 328, pp. 1682–1686.

Cavalier-Smith, T., 2006. Cell evolution and earth history: stasis and revolution. Philosophical Transactions of the Royal Society B, vol. 361, pp. 969–1006.

Chela-Flores, J., 2006. The sulphur dilemma: Are there biosignatures on Europa's icy and patchy surface? International Journal of Astrobiology, vol. 5, no. 1, pp. 17–22.

Chyba, C.F., and Phillips, C.B., 2002. Europa as an abode of life. Origins of Life and Evolution of the Biosphere, vol. 32, pp. 47–68.

Doolittle, W.F., and Papke, R.T., 2006. Genomics and the bacterial species problem. Genome Biology, vol. 7, art. 116, 7 pp.

Douglas, S., 2005. Mineralogical footprints of microbial life. American Journal of Science, vol. 305, pp. 503–525.

Drushel, G.K., Baker, B.J., Gihring, T.M., and Banfield, J.F., 2004. Acid mine drainage biogeochemistry at Iron Mountain, California, 2004. Geochemical Transactions, vol. 5, no. 2, pp. 13–32.

Falkowski, P.G., Fenchel, T., and Delong, E.F., 2008. The microbial engines that drive Earth's biogeochemical cycles. Science, vol. 320, pp. 1034–1039.

Falkowski, P.G., and Godfrey, L.V., 2008. Electrons, life and the evolution of Earth's oxygen cycle. Philosophical Transactions of the Royal Society B, vol. 363, pp. 2705–2716.

Flores, J.C., 2006. The sulfur dilemma: Are there biosignatures on Europa's icy and patchy surface? International Journal of Astrobiology, vol. 5, no. 1, pp.17–22.

Friedrich, C.G., Rother, D., Bardischewsky, F., Quentmeier, A., and Fischer, J., 2001. Oxidation of reduced inorganic sulfur compounds by bacteria: Emergence of a common mechanism? Applied and Environmental Microbiology, vol. 67, no. 7, pp. 2873–2882.

Gaidos, E.J., Nealson, K.H., and Kirschvink, J.L., 1999. Life in ice-covered oceans. Science, vol. 284, no. 5420, pp. 1631–1633.

Gaucher, E.A., Kratzer, J.T., and Randall, R.N., 2010. Deep phylogeny: how a tree can help characterize early life on Earth. Cold Spring Harbor Perspectives on Biology, 16 pp., 2a002238.

Gioia, G., Chakraborty, P., Marshak, S., and Kieffer, S.W., 2007. Unified model of tectonics and heat transport in a frigid Enceladus. Proceedings of the National Academy of Sciences USA, vol. 104, no. 34, pp. 13578–13581.

Guevremont, J.M., Bebie, J., Elsetinow, A.R., Strongin, D.R., and Schoonen, M.A.A., 1998. Reactivity of the (100) plane of pyrite in oxidizing gaseous and aqueous environments: effects of surface imperfections. Environmental Science and Technology, vol. 32, no. 23, pp. 3743–3748.

Gurnett, D.A., 2009. The search for life in the solar system. Transactions of the American Clinical and Climatological Association, vol. 120, pp. 299–325.

Hanczyc, M.M., Fujikawa, S.M., and Szostak, J.W., 2003. Experimental models of primitive cellular compartments: encapsulation, growth, and division. Science, vol. 302, pp. 618–622.

Hansma, H., 2008. Mica, bioenergetics and the origin of life. Biophysical Journal, vol. 94, no. 14.

Hayes, J.M., and Waldbauer, J.R., 2006. The carbon cycle and associated redox processes through time. Philosophical Transactions of the Royal Society B, vol. 361, pp. 931–950.

Hazen, R.M., and Sverjensky, D.A., 2010. Mineral surfaces, geochemical complexities, and the origins of life. Cold Spring Harbor Perspectives in Biology, 21 pp., 2:a002162.

Kasting, J.F., and Ono, S., 2006. Palaeoclimates: the first two billion years. Philosophical Transactions of the Royal Society B, vol. 361, pp. 917–929.

Keller, M., and Hettich, R., 2009. Environmental proteomics: a paradigm shift in characterizing microbial activities at the molecular level. Microbiology and Molecular Biology Review, vol. 73, no. 1, pp. 62–70.

Kerr, R.A., 2009. Tang hints of a watery interior for Enceladus. Meeting Briefs, American Geophysical Union, December, 15–19, 2008. Science, vol. 323, pp. 458–459.

Kieffer, S.W., and Jakosky, B.M., 2008. Enceladus: oasis or ice ball? Science, vol. 320, pp. 1432–1433.

Kieffer, S.W., Lu, X., Bethke, C.M., Spencer, J.R., Marshak, S., and Navrotsky, A., 2006. A clathrate reservoir hypotheses for Enceladus south polar plume. Science, vol. 314, pp. 1764–1766.

Kivelson, M.G., Khurana, K.K., Russell, C.T., Volwerk, M., Walker, R.J., and Zimmer, C., 2000. Galileo magnetometer measurements: a stronger case for a subsurface ocean at Europa. Science, vol. 289, pp. 1340–1343.

Lanoil, B.D., Sassen, R., La Duc, M.T., Sweet, S.T., and Nealson, K.H., 2001. Bacteria and archaea physically associated with Gulf of Mexico gas hydrates. Applied and Environmental Microbiology, vol. 67, no. 11, pp. 5143–5153.

Levy, M., and Miller, S.L., 1998. The stability of the RNA bases: implications for the origin of life. Proceedings of the National Academy of Sciences USA, vol. 95, pp. 7933–7938.

Lorenz, R.D., Stiles, B.W., Kirk, R.L., Allison, M.D., del Marmo, P., Less, L., Lunine, J.I., Ostro, S.J., and Hensley, S., 2008. Titan's rotation reveals an internal ocean and changing zonal winds. Science, vol. 319, pp. 1649–1651.

Lunine, J.I., 2006. Physical conditions on the early Earth. Philosophical Transactions of the Royal Society B, vol. 361, pp. 1721–1731.

Luo, H., Shen, L., Yin, H., Li, Q., Chen, Q., Luo, Y., Liao, L., Qiu, G., and Liu, X., 2009. Comparative geonomic analysis of *Acidithiobacillus ferrooxidans* strains using the *A. ferrooxidans* ATCCd 23270 whole-genome oligonucleotide microarray. Canadian Journal of Microbiology, vol. 55, no. 5, pp. 587–598.

Macalady, J., and Banfield, J.F., 2003. Molecular geomicrobiology: genes and geochemical cycling. Earth and Plantetary Science Letters, vol. 209, pp. 1–17.

Martin, W., and Russell, M.J., 2003. On the origins of cells: a hypothesis for evolutionary transitions from abiotic geochemistry to chemoautrophic prokaryotes, and from prokaryotes to nucleated cells. Philosophical Transactions of the Royal Society B, vol. 358, no. 1429, pp. 59–83.

Mathur, J., Bizzoco, R.W., Ellis, D.G., Lipson, D.A, Poole, A.W., Levine, R., and Kelley, S.T. 2007. Effects of abiotic factors on the phylogenetic diversity of bacterial communities in acidic thermal springs. Applied and Environmental Microbiology, vol. 73, no. 8, pp. 2612–2623.

McEwen, A.S., Ojha, L., Dundas, C.M., Mattson, S.S., Byrne, S., Wray, J.J., Cull, S.C., Murchie, S.L., Thomas, N., and Gulick, V.C., 2011. Seasonal flows on warm Martian slopes. Science, vol. 333, pp. 740–743.

McGuire, M.M., Edwards, K.J., Banfield, J.F., and Hamers, R.J., 2001. Kinetics, surface chemistry, and structural evolution of microbial mediated sulfide mineral dissolution. Geochimica et Cosmochimica Acta, vol. 65, no. 8, pp. 1243–1258.

McKay, C.P., 2010. An origin of life on Mars. Cold Spring Harbor Perspectives in Biology, 7 pp., 2a003509.

Mikucki, J.A., and Priscu, J.C., 2007. Bacterial diversity associated with Blood Falls, a subglacial outflow from the Taylor glacier, Antarctica. Applied and Environmental Microbiology, vol. 73, no. 12, pp. 4029–4039.

Morris, R.V., Ruff, S.W., Gellert, R., Ming, D.W., Arvidson, R.E., Clark, B.C., Golden, D.C., Siebach, K., Klingelhofer, G., Schroder, C., Fleischer, I., Yen, A.S., and Squyres, S.W., 2010. Identification of carbonate-rich outcrops on Mars by the *Spirit* rover. Science, vol. 329, pp. 421–424.

Newman, D.K., and Banfield, J.F., 2002. Geomicrobiology: how molecular-scale interactions underpin biogeochemical systems. Science, vol. 296, pp. 1071–1077.

Orgel, L.E., 2000. Self-organizing biochemical cycles. Proceedings of the National Academy of Sciences USA, vol. 97, no. 23, pp. 12503–12507.

Osterloo, M.M., Hamilton, V.E., Banfield, J.L., Glotch, T.D., Baldridge, A.M., Christensen, P.R., Tornabene, L.L., and Anderson, F.S., 2008. Chloride-bearing materials in the southern highlands of Mars. Science, vol. 319, pp. 1651–1654.

Pace, N.R., 1997. A molecular view of microbial diversity and the biosphere. Science, vol. 276, pp. 734–740.

Perrault, N.N., Anderson, D.T., Pollard, W.H., Greer, C.W., and Whyte, L.G., 2007. Characterization of the prokaryotic diversity in cold saline perennial springs of the Canadian high arctic. Applied and Environmental Microbiology, vol. 73, no. 5, pp. 1532–1543.

Perreault, N.N., Greer, C.W., Andersen, D.T., Tille, S., Lacrampe-Couloume, G., Lollar, B.S., and Whytle, L.G., 2008. Heterotrophic and autotrophic microbial populations in cold perennial springs of the high arctic. Applied and Environmental Microbiology, vol. 74, no. 22, pp. 6898–6907.

Philippot, P., Van Zuilen, M., Lepot, K., Thomazo, C., Farquhar, J., and Van Kranendonk, M.J., 2007. Early archaean microorganisms preferred elemental sulfur, not sulfate. Science, vol. 317, pp. 1534–1537.

Pisapia, C., Chaussidon, M., Mustin, C., and Humbert, B., 2007. O and S isotopic composition of dissolved and attached oxidation products of pyrite by *Acidithiobacillus ferrooxidans:* comparison with abiotic reactions. Geochimica et Cosmochimica Acta, vol. 71, pp. 2474–2490.

Price, P.B., and Sowers, T., 2004. Temperature dependence of metabolic rates for microbial growth, maintenance, and survival. Proceedings of the National Academy of Sciences USA, vol. 101, no. 13, pp. 4631–4636.

Rawlings, D.E., and Kusano, T., 1994. Molecular genetics of *Thiobacillus ferroxidans*. Microbiological Reviews, vol. 58, no. 1, pp. 39–55.

Reed, D.W., Fujita, Y., Delwiche, M.E., Blacwelder, D.B., Sheridan, P.P., Uchida, T., and Colwell, F.S., 2002. Microbial communities from methane hydrate-bearing deep marine sediments in a forearc basin. Applied and Environmental Microbiology, vol. 68, no. 8, pp. 3759–3770.

Rimstidt, D.J., and Vaughan, D.J., 2003. Pyrite oxidation: a state-of-the-art assessment of the reaction mechanism. Geochimica et Cosmochimica Acta, vol. 67, no. 5, pp. 873–880.

Rohde, R.A., and Price, B., 2007. Diffusion-controlled metabolism for long-term survival of single isolated microorganisms trapped within ice crystals. Proceedings of the National Academy of Sciences USA, vol. 104, no. 42, pp. 16592–16597.

Russell, M.J., and Hall, A.J., 1997. The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. Journal of the Geological Society, London, vol. 154, pp. 377–402.

Sattley, W.M., and Madigan, M.T., 2006. Isolation, characterization, and ecology of cold-active, chemolithotrophic, sulfur-oxidizing bacteria from perennially ice-covered Lake Fryxell, Antarctica. Applied and Environmental Microbiology, vol. 72, no. 8, pp. 5562–5568.

Schafer, G., Engelhard, M., and Muller, V., 1999. Bioenergetics of the archaea. Microbiology and Molecular Biology Reviews, vol. 63, no. 3, pp. 570–620.

Schippers, A., and Jorgensen, B.B., 2001. Oxidation of pyrite and iron sulfide by manganese dioxide in marine sediments. Geochimica et Cosmochimica Acta, vol. 65, no. 6, pp. 915–922.

Shen, Y., Farquhar, J., Masterson, A., Kaufman, A.J, and Buick, R., 2009. Evaluating the role of microbial sulfate reduction in the early Archean using quadruple isotope systematics. Earth and Plantary Science Letters, vol. 279, pp. 383–391.

Singer, P.P., and Stumm, W., 1970. Acidic mine drainage: the rate determining step. Science, vol. 167, pp. 1121–1123.

Singer, E., Webb, E.A., Nelson, W.C., Heidelberg, J.F., Ivanoca, N., Pati, A., and Edwards, K.J., 2011. Genomic potential of *Marinobacter aquaeolei*, a biogeochemical "opportunitroph." Applied and Environmental Microbiology, vol. 77, no. 8, pp. 2763–2771.

Sleep, N.H., 2010. The hadean–archaean environment. Cold Spring Harbor Perspectives in Biology, 14 pp., 2:a002527.

Sleep, N.H., and Bird, D.K., 2008. Evolutionary ecology during the rise of dioxygen in the Earth's atmosphere. Philosophical Transactions of the Royal Society B, vol. 363, pp. 2651–2664.

Smith, J.V., Arnold, F.P., Jr., Parsons, I., and Lee, M.R., 1999. Biochemical evolution III: polymerization on organophilic silica-rich surfaces, crystal-chemical modeling, formation of first cells, and geological clues. Proceedings of the National Academy of Sciences USA, vol. 96, pp. 3479–3485.

Sotin, C., and Tobie, G., 2008. Titan's hidden ocean. Science, vol. 319, pp. 1629–1630.

Spencer, J.R., Barr, A.C., Esposito, L.W., Helfenstein, P., Ingersoll, A.P., Jaumann, R., McKay, C.P., Nimmo, F., Porco, C.C., and Waite, J.H., 2009. Enceladus: an active cryovolcanic satellite. In: Saturn After Cassini/Huygens, M.K. Dougherty et al., eds. Springer-Verlag, New York, pp. 683–724.

Spitzer, J., and Poolman, B., 2009. The role of biomacromolecular crowding, ionic strength, and physicochemical gradients in the complexities of life's emergence. Microbiology and Molecular Biology Reviews, vol. 73, no. 2, pp. 371–388.

Stetter, K.O., 2006. Hyperthermophiles in the history of life. Philosophical Transactions of the Royal Society B, vol. 361, pp. 1837–1843.

Takai, K., Nakamura, K., Toki, T., Tsunogai, U., Miyazaki, M., Miyazaki, J., Hirayama, H., Nakagawa, S., Nunoura, T., and Horikoshi, K., 2008. Cell proliferation at 122°C and isotopically heavy CH_4 production by a hyperthermophilic methanogen under high-pressure cultivation. Proceedings of the National Academy of Sciences USA, vol. 105, no. 31, pp. 10949–10954.

Teolis, B.D., Jones, G.H., Miles, P.F., Tokar, R.L., Magee, B.A., Waite, J.H., Roussos, E., Young, D.T., Crary, F.J., Coates, A.J., Johnson, R.E., Tseng, W.-L., and Bargiola, R.A., 2010. Cassini finds an oxygen-carbon dioxide atmosphere at Saturn's icy moon Rhea. Science, vol. 330, pp. 1813–1815.

Tung, H.C., Bramall, N.E., and Price, P.B., 2005. Microbial origin of excess methane in glacial ice and implications for life on Mars. Proceedings of the National Academy of Sciences USA, vol. 102, no. 51, pp. 18292–18296.

U.S. Environmental Protection Agency, 2003. Contaminant Candidate List: Regulatory Determination Support Document for Sulfate. EPA-815-R-03-16. U.S. EPA, Office of Water (4607M), Standards and

Risk Management Division, Washington, DC.
http://www.epa.gov/SAFEWATER/ccl/cclregdetermine.html. 56 pp.

Vasas, V., Szathmary, E., and Santos, M., 2010. Lack of evolvability in self-sustaining autocatalytic networks constraints metabolism: first scenarios for the origin of life. Proceedings of the National Academy of Sciences USA, vol. 107, no. 4, pp. 1470–1475.

Wacey, D., Saunders, M., Brasier, M.D., and Kilburn, M.R., 2011. Earliest microbially mediated pyrite oxidation in ~3.4 billion-year-old sediments. Earth and Planetary Science Letters, vol. 301, pp. 393–402.

Wachtershauser, G., 1990. Evolution of the first metabolic cycles. Proceedings of the National Academy of Sciences USA, vol. 87, pp. 200–204.

Wachtershauser, G., 1994. Life in a ligand sphere. Proceedings of the National Academy of Sciences USA, vol. 91, pp. 4283–4287.

Whitman, W.B., 2009. The modern concept of the procaryote. Journal of Bacteriology, vol. 191, no. 7, pp. 2000–2005.

Wolfe-Simon, F., Blum, J.S., Kulp, T.R., Cordon, G.W., Hoeft, S.E., Pett-Ridge, J., Stolz, J.F., Webb, S.M., Weber, P.K., Davies, P.C.W., Anbar, A.D., and Oremland, R.S., 2010. A bacterium that can grow by using arsenic instead of phosphorus. ScienceExpress, research article, http://www.sciencexpress.org/2 December 2010/ Page 1/10.1126/science.1197258.

Zolotov, M.Y., and Shock, E.L., 2004. A model for low-temperature biogeochemisty of sulfur, carbon, and iron on Europa. Journal of Geophysical Research, vol. 109, E06003, 16 pp.

PART II
ASSESSMENT OF ACID MINE DRAINAGE, ROCK DRAINAGE, AND SULFATE SOILS

8
Sampling Strategies for Acid Drainage Studies

JAMES A. JACOBS

As part of the initial environmental site inspection of a property to obtain background information, it is necessary to document the setting, physical and environmental characteristics, current and historical, property boundaries, historical mining operations, site ownership, mine or facility ownership (if different from land ownership), mine waste management practices, previous site inspection reports, regulatory permits, previous site investigation reports, and geotechnical reports, together with data on zoning, regulatory status, current land use, and adjacent and nearby land use. Regulatory agencies may have files on properties that might include permits, inspection reports, development plans, mining plans, waste discharge permits, mine closure plans, and site closure documents. During the site inspection, all features should be photographed and documented properly. Interviews with owners, operators, and employees should occur to verify site history and waste management practices.

Environmental Site Inspection

The following mine features associated with mine sites should be documented: all buildings, structures, and processing areas, including shafts and open pits (Department of Toxic Substances Control, 1998). Locations of all underground workings should be noted on maps based on interviews with knowledgeable persons on site: tunnels, shafts, adits, stopes, raises, glory holes, and ventilation shafts. Unsupported underground mine features are dangerous and should not be entered except by properly trained personnel. Potential physical hazards and chemicals are used in mine processing (cyanide, mercury, etc.), fueling of vehicles and equipment (gasoline, diesel, or kerosene), or lubricating and cleaning equipment (chlorinated solvents). All mine waste piles should be identified and mapped to determine the approximate size and volume of the disturbed areas. Part of the inspection is to determine if acid drainage is occurring, so noting and taking photographs to document site conditions is appropriate. Acid drainage can be identified by discoloration of the soil or rock outcrops, crystal formation on soil or rock surfaces, abrupt changes in vegetation, or stressed, dead, or absent vegetation.

In creeks, a pH meter or pH paper will help to establish quickly if acid drainage is present. Fish kills, or dead aquatic organisms or their absence, are another indication that acid drainage may be present. During the site inspection, determine if the land use observed is consistent with the land use identified in the background research and historical records search. Note the site location relative to uninhabited and undeveloped areas. Correlate significant features on site to the site map and historical aerial photographs, if available. Review historical aerial photographs for each decade, going back as far as photos are available. In some cases, historical aerial photographs of some areas date back to the 1920s and 1930s. Historical societies might also have historical photographs and maps.

Sampling strategies can be used for acid drainage studies to get the most out of laboratory budgets and to obtain representative analytical data. Decision units are significantly a part of this strategic evaluation. Discrete, composited, and multi-increment sampling for soil and water are distinctly different, with benefits and disadvantages for each method. Selecting the proper sampling method can optimize project success by meeting technical objectives and budget goals.

Decision Units

To have successful acid drainage evaluations, the sample data must be representative of the pH, iron, sulfides, various types of sulfur, total carbon, total sulfur, total nitrogen concentrations, total metals, leachable metals, and so on. A decision unit is an area or volume of soil, sediment, or rock where samples are to be collected and decisions made based on the resulting data. The variability within the decision unit needs to be captured in the data but not determined specifically. The decision units may be associated with a particular media layer in vertical and lateral extent, with specific pH, sulfide or iron content, and so on.

The decision unit delineation is dependent on the data quality objectives for the acid drainage project. Once the decision unit boundaries are defined, multiple-increment subsamples or aliquots can be collected within the decision units. Multiple-increment samples may be collected within a single decision unit, but a multiple-increment sample should not be collected across more than one decision unit.

Sampling Strategies

There are several approaches to soil and water sampling: (1) discrete sampling, (2) composite sampling, and (3) multiple-increment sampling. The discrete sample provides a specific sample location, and the laboratory results from that sample can be assigned to that specific location and depth. Compositing might use four discrete samples, and the soil cores are either mixed in a clean bucket in the field or in the laboratory. Only one composited sample, which is a combined mixture of the four samples, is actually analyzed in the laboratory, which saves costs but does not provide necessarily representative or repeatable data. The laboratory results are an average of the four samples. Given the small number of samples in the composite, one sample with an excessively high sulfur content will bias the results, even though the other three samples might had sulfur concentrations below the detection level.

Multiple-increment sampling is not the same as simple composite sampling. A multiple-increment sample is collected within a decision unit, whereas a composite may be collected without regard to a specific decision unit. Unlike multiple-increment sampling, composite sampling results are not necessarily repeatable and representative. A composite sample is a simple combination of discrete samples. A multiple-increment sample is a representative sample for a given decision unit. Although the physical process of collection is similar, the information derived from each process is different. As such, composite sampling cannot provide representative decision unit population data (Department of Environmental Conservation, 2009). More information on multiple-increment sampling is available (Interstate Technology and Regulatory Council, 2011).

Multiple-increment sampling has been used successfully on military reservations, where the objective of the studies is to evaluate the presence or absence of munitions and explosives of concern. Interestingly, the spatial arrangement of the impact from explosives can be similar to the somewhat random distribution of heavy metals or iron sulfides in mine overburden waste piles. Once the chemical analyses are determined based on the history of the site, the goal of subsurface investigations are to evaluate any materials originating from unexploded ordnance, discarded military munitions, or other military munitions, including explosive and nonexplosive materials, and any munitions breakdown products. Since the main objectives of such military studies are to evaluate whether or not further response action is needed, the main goal of multiple-increment sampling is to adequately assess the presence or absence of the contaminant, and to assess whether there is or is not a threat to human health or the environment. The analogy to military challenges of unexploded ordnance is similar to the spatial challenges facing mining

companies unearthing overburden and placing the waste rocks in vast surface piles. Some areas of the large piles may be relatively low in pyrite and metals concentrations, and other areas may be quite high, posing a significant threat to human health and the environment. Using the multi-increment sampling method on large mining waste stockpiles, some areas will be high-graded and other piles will be determined not to pose an environmental threat. This reproducible sampling method within decision units provides the technical confidence that should a resampling event be requested by regulatory agencies, similar analytical results will be obtained.

Discrete sampling programs for acid drainage studies are generally simple, fast, and generally familiar, with specific depth and location recorded for each sample and a specific chemical analysis. The discrete sampling method can be performed on a tight grid and used to identify the worst-affected areas that might cause or have existing acid drainage. The disadvantage of discrete sampling programs is that an inadequate number of soil or groundwater samples is likely to be collected, resulting in samples that might not be truly representative of the conditions or contaminant levels of soil or water. Discrete sampling programs also tend to have a high analytical cost for the data obtained. For acid drainage studies, discrete location field measurements for water, including pH, dissolved oxygen oxidation–reduction potential, temperature, and conductivity, would be appropriate. Field colorimetric analysis of various metals, including iron and sulfur analyses, would best be done on a discrete basis. However, averaging the acid drainage–associated metals concentrations, total carbon percent, total sulfur percent, and total nitrogen percent over a large decision unit such as a particular waste tailing pile, multiple-increment sampling for the associated metals might be an appropriate way to get defensible, reproducible laboratory data that would highlight the average concentrations and not the hot spots.

Inadequate sample coverage results in poor lithological or geochemical characterization of the decision units. Too often in the past there has been an unnecessary focus on hot spots for risk assessment and remediation, reflecting the variability of the concentrations, not the average health exposure or average cost for remediation. For neutralization at acid drainage sites, if the lowest pH values were used rather than the average pH value, the costs estimated for liming could be incorrect by several orders of magnitude. Replicate samples to verify accuracy are almost never collected (Brewer and Broderson, 2006).

Multiple-increment sampling for acid drainage studies is a sampling method used to obtain representative samples. Previously, to get representative metals concentrations within the study boundaries, the investigator could either select the maximum concentration or derive a representative metals concentration by calculating the 95% upper confidence limit (UCL) of the mean. In the past, each methodology relied on the use of discrete samples (Ohio EPA, 2007).

If the site decision unit is represented by a single multiple-increment sample, the multiple-increment sample provides an estimate of central tendency concentrations and thus may eliminate the need for further statistical analysis of the data, such as calculating the 95% UCL of the mean. As an example, for metals associated with the coal or hardrock mining waste rocks, the multiple-increment sampling will provide representative metal concentrations. These data are important for estimating metals' leaching potential over the entire decision unit.

Most acid drainage sites need to be broken down into areas about which a decision needs to be made regarding the extent and magnitude of potential or actual acid drainage and how to achieve applicable standards. The multiple-increment method provides the investigator with a more accurate and reproducible estimate of average acid drainage potential and metals concentrations across the decision unit. Multiple-increment theory also states that the method increases the probability of assessing potential “hot spots” that may have been missed during conventional discrete sampling (Ohio EPA, 2007).

Multiple-increment sampling is a more rigorous form of sampling that is designed to generate a result that is reproducible and defensible. Traditional composite sampling generates a result that may be close to average concentration but is not necessarily reproducible. A critical aspect and prerequisite for multiple-increment sampling is defining the decision unit. A decision unit can be the area or exposure unit identified, or both. An identified area or exposure area can also include multiple decision units. Generally, a decision unit is not considered to be larger than ¼ acre. Decision units are restricted to actual source zones and must not incorporate large, uncontaminated areas. In an acid drainage study, a decision unit might include a particular waste pile but not the road leading to the waste pile or the creek on the other side of the waste pile. Other waste piles or ore-processing areas would probably be separate decision units. The decision unit delineation, although helpful, is not a critical prerequisite for discrete sampling. The decision as to which discrete samples are to be included within a specific identified area or exposure unit can be made at a later stage when demonstrating that applicable regulatory standards are met in the area or exposure unit identified (Ohio EPA, 2007).

Statistically, multiple-increment samples cannot be included with discrete samples as a single data set to calculate a representative concentration across the decision unit. This approach would bias discrete samples more heavily in the data set, and the resulting concentration might be more biased toward the average concentration of the discrete samples.

A traditional composite sample is a combination of discrete samples. Typically, during a standard composite sampling project, an investigator will grid off an area and collect a number of samples within the grid. For a multiple-increment sampling project, the sample is one that is comprised of multiple aliquots, frequently dozens, which are collected randomly from the decision unit, typically less than ¼ acre. The aliquots are collected randomly to avoid sampler bias. In areas within the decision unit that visibly or potentially may contain elevated spots, a discrete soil or water sample may be warranted.

An effective, inexpensive, and easy method of locating aliquot locations is the *random walk method*. In this approach, the sample collector wanders over the decision unit and randomly grabs a small aliquot of soil. Typically, a stainless steel ⅞-in. step probe is used to collect the surface soil. The depth of the increment is decided on a decision unit-by-decision unit basis and should be part of the sampling design process. Generally, a minimum of 30 increments should be collected in the decision unit. If replicates yield a variability that is too great, the number of aliquots would have to be increased and more sample mass would be required.

Sample Processing

Traditional composite soil processing uses discrete soil samples that are placed in a container and mixed. A subset of this soil mixture is collected and sent to the laboratory for chemical analysis. Multiple-increment soil sampling requires specific postsample processing. Once a minimum of 30 aliquots are collected for the multiple-increment soil sample, the aliquots are combined and placed into a pan and dried. Subsequent multiple-increment sample processing can take place either in the field or in the lab. The sample is sieved (No. 10) and then ground to obtain a consistent particle size. The ground sample is laid out and another multiple-increment sample is collected to fill the soil sample container. Other methods to collect the final sample have been accepted, such as the *line and scoop method* (EPA 600/R-92/128).

Advantages for multiple-increment sampling include the fact that the results are independent of the sampler and the results are reproducible. The results are representative and can be extrapolated to locations not sampled, and the sample error can be estimated. Multiple-increment sampling has been used

extensively by the U.S. military for the analysis of explosives and most metals (Ohio EPA, 2007). The multiple-increment sampling method is appropriate to use to analyze total and soluble associated metals for acid drainage studies. The multiple-increment sample process includes sieving and grinding as part of the process, to ensure uniform sample particle size.

It may be necessary to balance mobilization and analytical costs when making sampling strategy decisions for acid drainage studies. Although multiple-increment sampling may require more field time and lab processing and preparation time, other analytical and statistical valuation costs for the acid drainage project may be reduced.

A composite sample is a collection of multiple discrete samples combined to form the sample, whereas a multiple-increment sample is one that is comprised of multiple aliquots that are combined and processed, either in the field or in the laboratory, to form the sample. Contrary to composite sampling, multiple-increment sampling produces results that are both reproducible and defensible. For more technical information on multiple-increment sampling, refer to reports of the U.S. EPA (1992, 2003) and the Ohio EPA (2007).

Multiple-increment sampling programs have two main components, field sampling and field measurements (pH, field colorimetric analysis of selected metals) or fixed laboratory analysis (metals by EPA methods). A multiple-increment sample combines many small increments of soil, surface water, or groundwater from a large number of sampling points across a defined decision unit. Multiple-increment sampling differs from typical composite sampling in two specific ways. The specific number of increments in multiple-increment sampling is significantly greater than that for discrete sampling. For example, a multiple-increment sampling program in a mine tailing pile of 5000 cubic yards might use 50 to 100 identically sized multiple-increment soil core samples. For the composite soil samples over the same soil volume, a series of 4 to 10 discrete samples might be used. For acid drainage studies, the amount of carbonate in the soil or rock pile, the amount of pyrite present, and the amount of organic material, for example, would be more representative using multiple-increment sampling than by discrete samples.

Each multiple-increment sample is based on an entire area of interest or decision unit. Theoretically, a multiple-increment sample minimizes single-sample variability that results from discrete sampling or composites using a small number of points, such as four. For example, a multiple-increment sample of approximately 1 kg of soil can be sent to a laboratory for processing in its entirety to help address compositional and distributional heterogeneity of the soil, saving time, and analytical costs, and the results will be representative of the decision unit and not focus on the one or two high-impact discrete samples. The multiple-increment sample replicates are typically normally distributed.

For field implementation of the multiple-increment sampling program, a specialized field soil multiple-increment sampling tool can be used to collect fixed-diameter cores of soil that are combined for each multiple-increment sample. Specific multiple-increment tools have interchangeable core barrels that collect soil from variable depths and of various diameters to maintain a desirable mass of about 1 kg. For water samples using multiple-increment sampling procedures, a fixed water volume is needed for each sample.

A multiple-increment sample is collected within a decision unit, whereas a composite may be collected without regard to a specific decision unit. Unlike multiple-increment sampling, composite sampling does not address sampling bias adequately. A composite sample is a simple combination of discrete samples. A multiple-increment sample is a representative sample for a given decision unit. Although the physical process of collection is similar, the information derived from each process is different. As such,

composite sampling cannot provide representative decision unit population data (Department of Environmental Conservation, 2009).

Multiple-Increment Sampling Theory

The objective of environmental sampling is to quantify particular geochemical characteristics of the media sampled, such as the pH of the groundwater or the amount of sulfide or iron present in soil at a given particular location at a site. Traditionally, environmental investigations have used discrete sampling to characterize environmental media. However, the number of discrete samples often collected at a site does not lend itself to statistically valid interpretation and cannot accurately quantify contaminant concentrations due to the heterogeneity of environmental media. For acid drainage studies of waste tailing piles, this is especially true, since the concentrations of the total and soluble metals may vary considerably and may relate to the original sulfur and iron concentrations in the hardrock ore body or pyrite in the vicinity of a coal seam. Since unearthing and removal of the waste rocks surrounding an ore body or coal seam may tend to be haphazard, the concentrations of acid-generating components may be placed in the waste tailing piles in an unorganized and undocumented manner, and concentrations of the associated metal wastes may not be related to specific location in the waste storage units.

Therefore, it is important to identify the true mean concentration of a population of metals concentrations without the census of every data point. In the case of a 30,000-yd^3 waste rock stockpile, for example, the entire mass would have to be analyzed to determine the true mean concentration of particular metals. Since it is impossible to sample and analyze the entire population, due to practical considerations and cost limitations, statistical methods are used to determine a representative concentration. A theory of particulate sampling was developed by geologist Pierre Gy to improve the quality of data gathered in support of mineral exploration and mining (Pitard, 1993). The multiple-increment approach described herein is based on Gy's theories and is applicable to environmental sampling at contaminated sites (Department of Environmental Conservation, 2009).

Sources of Error

Heterogeneity at acid drainage sites exists in metal contaminant levels, various possible iron and sulfur combinations, and variations in soil or rock types. A portion of sampling error is a result of compositional and distributional heterogeneity. Compositional heterogeneity describes the variability of contaminant concentrations between the particles that make up the population. This type of heterogeneity results in fundamental error. Fundamental error is a result of not representing proportional concentrations of all of the particles in the population. To minimize fundamental error, it is imperative that enough mass be collected and analyzed to represent all particles in the exact proportion found in the population.

Distributional heterogeneity occurs when particles sizes or contaminant levels are not distributed randomly across the population, due to slight spatial variations. Waste piles of mining waste rocks or ore processing wastes vary in concentrations of the waste metals and pH potential, as well as having lithologic variability. Spatial variability will be missed if all samples are collected from one place. This type of heterogeneity results in grouping and segregation error. To minimize such error, it is imperative to collect sample increments randomly and in enough locations to capture the spatial variability. Multiple-increments control these two major types of sampling error in most situations. Grouping and segregation error is controlled by collecting multiple randomly located sample increments to address distributional heterogeneity. In general, a minimum of 30 to 50 random increments are required to address grouping and

segregation error. If greater distributional heterogeneity is expected, more increments would be required (Department of Environmental Conservation, 2009). Planning out the best sampling strategy for an acid drainage project will help to provide representative and repeatable laboratory data sets.

References and Suggested Reading

Brewer, R., and Broderson, J., 2006. Use of multi-increment samples and decision units to optimize site investigation, assessment and remediation. Presentation notes for a workshop for the Association for the Environment Health and Sciences, San Diego Conference.

Department of Environmental Conservation, 2009. Draft Guidance on Multi-Increment Soil Sampling. State of Alaska, Division of Spill Prevention and Response, Contaminated Sites Program, Juneau, AK, 17 pp.

Department of Toxic Substances Control, 1998. Abandoned Mine Lands Preliminary Assessment Handbook. State of California, Environmental Protection Agency, DTSC, Sacramento, CA, 149 pp.

Ohio EPA, 2007. Multi-incremental Sampling for Soils and Sediments. Standard Operating Procedure 2.6.1. Ohio EPA, Division of Emergency and Remedial Response, Columbus, OH.

Interstate Technology and Regulatory Council, 2011. Incremental Sampling Methodology. Draft. ITRC, Washington, DC.

Pitard, F.F., 1993. Pierre Gy's Sampling Theory and Sampling Practic: Heterogeneity, Sampling Correctness, and Statistical Process Control. CRC Press, Boca Raton, FL, 488 pp.

U.S. Environmental Protection Agency, 1992. Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies. EPA 600/R-92/128. U.S. EPA, Washington, DC.

U.S. Environmental Protection Agency, 2003. Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples. EPA/R-03/027. U.S. EPA, Washington, DC.

9
Stream Characterization for Acid Mine Drainage

JEFF SKOUSEN AND JAMES A. JACOBS

Stream characterization for acid mine drainage incorporates field observations and the collection of accurate data on the seep, stream, or water body that can be used to determine the extent and severity of the acid drainage issues. Although the water body in question can range from a seep to a river, lake, or bay system, for ease of use in this chapter we refer to all water characterization as stream sampling (lotic systems). Not only can stream characterization data be used to detect and document existing or potential acid rock generation, they can also be used to guide decisions about specific strategies for minimizing future impacts by locating acid generation sources, such as high concentrations of pyrite in soils, sediments, or rocks, as well as remediating the water and locating treatment systems for water quality improvement. Stream characterization involves chemical screening and sampling as well as water flow calculations. Watershed characterization for streams affected by acid mine drainage has been described by Skousen and Mains (1997).

Characterizing Streams for Acid Drainage

Assessing water quality as part of an acid mine drainage evaluation includes field measurements of chemical parameters and might include fixed laboratory analysis. The field measurements usually rely on various portable instruments or field kits (test strips, colorimetric methods, or titration methods). Characterization of acid generation sources includes hillside seeps (Figure 9.1), where water flow may be seasonal.

FIGURE 9.1 A source of acid drainage can be as small as a seep from a hillside. (Courtesy of J. Skousen.)

A variety of manufacturers make multiparameter water quality instruments. These devices typically measure two or three parameters (generally, temperature, pH, and/or electrical conductivity), but some of the more advanced portable field instruments measure numerous parameters, including: pH, electrical conductivity, dissolved oxygen, oxidation–reduction potential, salinity, saltwater specific gravity, temperature, total dissolved solids, and turbidity. The tests commonly conducted for acid drainage studies at stream sampling sites are described in detail below.

pH

The measurement and understanding of pH is of great importance in acid drainage studies. The pH of water gives an indication of the general chemical status of the water. It is an expression of the hydrogen-ion activity or concentration in the water and is approximately related to the molarity of H^+ by $pH = -\log[H^+]$. A pH of 7 is considered neutral. Water pH below 7 is considered acidic; pH above 7 is alkaline or basic. Since the scale is logarithmic, for each unit change in pH, there is a tenfold change in acid strength. For example, water with a pH of 5 is 10 times more acidic than water with a pH of 6. A pH of 4 is 100 times more acidic than a pH of 6. For most common liquids, the pH scale is from 0 to 14, with 0 being the general lower end of the acidic range, 7 considered neutral water, and 14 being the upper end of the caustic or alkaline range. In areas with extreme acid drainage conditions, the 0 to 14 pH scale commonly used does not always work. In fact, negative pH values do occur, as the Richmond mine case study illustrates (see later).

In the study of chemistry, an acid is a compound that donates protons or hydrogen ions (H^+) and usually accepts electrons. An acid has more free hydrogen ions (H^+) than hydroxyl ions (OH^-), so the pH is below 7.0. How easily the proton or hydrogen ion is released from the compound into the water is an indication of the strength of the acid. Sulfuric acid, the acid produced from acid drainage, is a strong acid compared to acetic acid (commonly called vinegar), which is a weak acid. Even a few molecules of sulfuric acid in water give up their hydrogen ions readily, so sulfuric acid is considered a strong acid. The concentration of the acid reflects the number of molecules in the solution, so a high concentration of sulfuric acid might be 50% concentration. The higher the concentration of an acid, the lower the pH value. The pH scale is shown in Figure 9.2. A pH level of 7.0 at 25°C is defined as neutral because the concentration of H_3O^+ equals the concentration of OH^- in pure water.

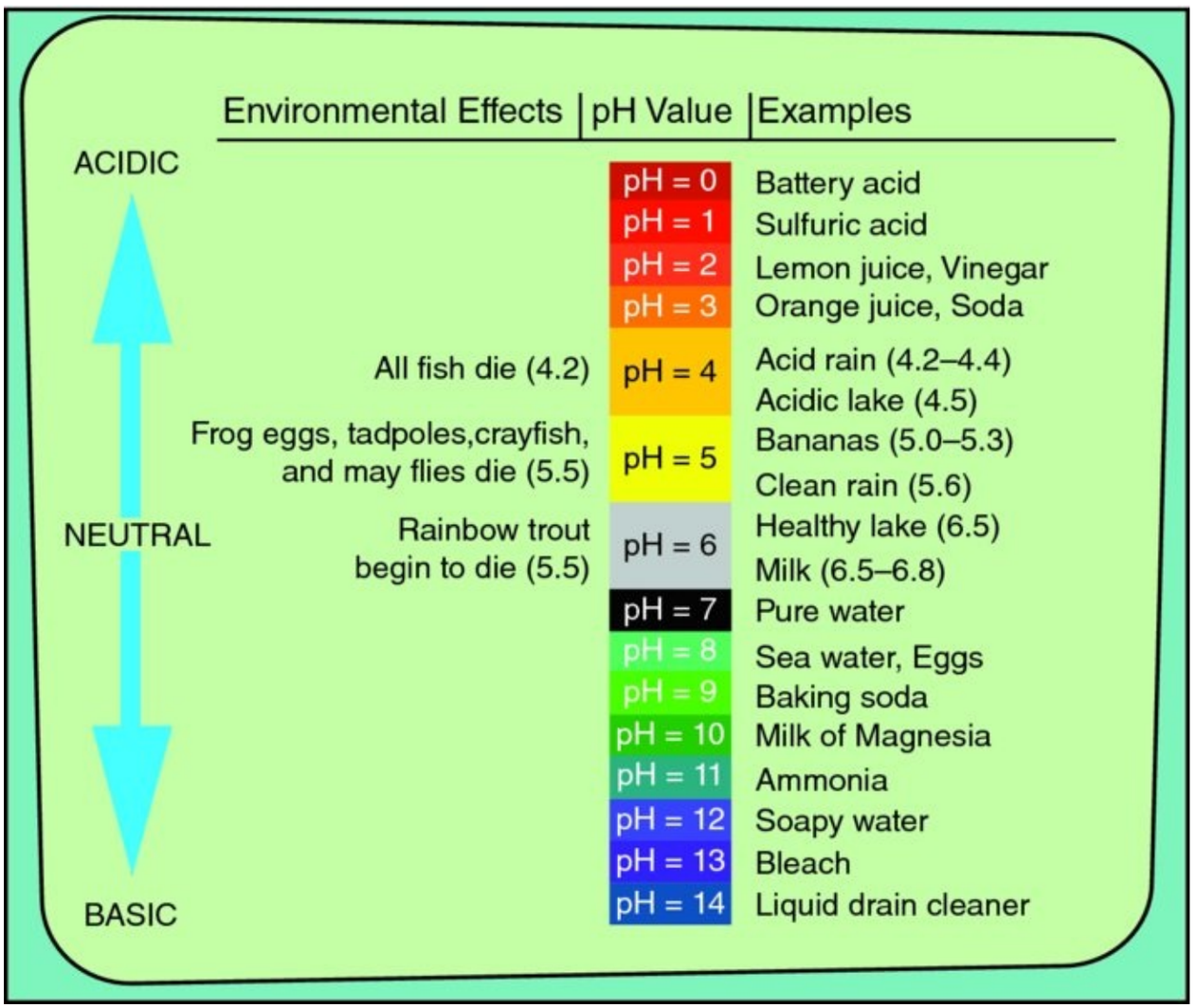


FIGURE 9.2 A pH scale with examples from common products and some environmental effects related to acidic drainage. (U.S. EPA, http://www.epa.gov/acidrain/education/site_students/images/phscale.gif.)

An example of how pH is calculated for strong acids illustrates the relationship between pH and acid concentration. A 12 molar (M) solution of an extremely strong acid (assuming that 100% of the acid is ionized) gives 12 mol/L of H_3O^+. Sulfuric acid (H_2SO_4), the acid generated during the pyrite oxidation processes, has two protons for release. There is also a small contribution from HSO_4^- generated from the first ionization step, which generates about 0.3795 mol/L of H_3O^+. Adding the 0.3795 mol/L to the 12 mol/L results in a total of 12.3795 mol/L. This would give a pH of −1.093. However, a strong acid is

100% ionized only if it forms a dilute solution which is, for example, no stronger than 0.1 M. For 12 M sulfuric acid, only an estimated 75% of the acid is actually ionized. Therefore, 0.75%×12 M = 9 mol/L. The amount actually ionized reduces the HSO_4^- by 25%, to 9 mol/L, and the H_3O^+ from that reaction would be reduced 25%, to about 0.3286 mol/L. Adding the 0.3286 mol/L and 9 mol/L results in 9.3286 mol/L and a pH calculated to be −0.97, which is still close to the 100% ionized calculation of −1.093. Rounded off, the 12 M solution of sulfuric acid is estimate to have a pH of −1.

When measuring the pH of strongly acidic solutions, systematic errors occur when employing commonly used measuring instruments such as glass pH electrodes. Without using special pH correction or calibration methods, the glass electrodes give pH readings that are consistently too high in strongly acidic solutions because there is so little water per acid unit. A similar systematic error occurs in extremely alkaline solutions where the glass electrode responds to the dissolved sodium ions as though they were hydrogen ions, giving a pH reading that is consistently too low for extremely high pH solutions.

Case Study: Negative pH

Although rare, for acid mine drainage studies, negative pH values have been well documented. Nordstorm et al. (2000) noted that extremely acidic mine waters with pH values as low as −3.6, total dissolved metal concentrations as high as 200 g/L, and sulfate concentrations as high as 760 g/L have been encountered underground in the Richmond mine at Iron Mountain near Redding, California. The drainage waters seeping from the Richmond mine are the most acidic waters on Earth. The negative pH measurements were obtained using the Pitzer method to define pH for calibration of the glass membrane electrodes. The calibration of pH below 0.5 with glass membrane electrodes becomes strongly nonlinear but is reproducible to a pH as low as −4. Numerous efflorescent minerals were found forming from these acid waters. These extremely acid waters were formed primarily by pyrite oxidation and concentration by evaporation, with minor effects from aqueous iron(II) or ferrous iron oxidation and efflorescent mineral formation (Nordstrom et al., 2000).

Water pH

Unlike the Iron Mountain EPA Superfund site, where negative pH values have been measured, the majority of acid drainage studies that most investigators will encounter will have positive pH numbers. A standard pH meter is probably the most common piece of field monitoring equipment used to evaluate acid drainage. A pH meter can be relatively inexpensive, costing well under $50, or they can be extremely expensive, up to $1000, depending on options such as waterproof housing and data storage capabilities. Since pH is sensitive to temperature, most pH meters have a temperature correction chart or knob to correct for variations in field temperature. pH meters, regardless of the type, should be cleaned and calibrated regularly and always at the start of the day on which they are being used. Calibrating involves adjusting the reading of the meter using pH standards, which are premixed solutions of known pH values, usually 4, 7, and 10. Care should always be taken to use calibration solutions within their stated shelf lives and to minimize the potential for dilution or cross-contamination.

When taking pH measurements in the field, if the pH of a stream is below 4.5, there is a strong probability that the water is contaminated by acid drainage. If a water source being measured is coming immediately out of the ground, the pH should be measured downstream after the water has had some time to become oxidized. Sometimes acid drainage coming directly from the ground may be in an unoxidized state and have a relatively high pH (5.0 to 6.5). Once the water is oxidized, the pH may drop to 3.0 or less.

Electrical Conductivity

Electrical conductivity, specific conductance, or conductivity is a measure of the ability of water to conduct an electrical current. Conductivity increases as more substances capable of conducting a current are dissolved in the water. Seawater contains sodium and chloride ions, both of which can conduct an electrical charge. Similar to acidic waters, saline waters can conduct electrical currents. Electrical conductivity is used to give an approximation of the amount of solids dissolved in water. Usually, contaminated water has a higher conductivity value than that of uncontaminated water. Water containing acid drainage produces noticeably elevated conductivity readings since the dissolved metals, sulfate, and hydrogen ions can all conduct an electrical charge.

Electrical conductivity bridges (or meters) are rugged pieces of equipment that are useful in the field. The readings can be collected quickly and the meters are easy to use. The source of acid drainage can be located quickly by taking numerous electrical conductivity and pH readings while moving up a stream or water body. If the electrical conductivity readings gradually decline and pH increases, this indicates a diffuse nonpoint source of acid drainage entering the stream or water body. If the conductivity readings stay high and the pH stays low but then the conductivity drops suddenly and the pH increases suddenly, this indicates that the source of acid drainage has been passed. By backtracking in the field, the source of acid drainage should be easy to locate using a conductivity meter in combination with a pH meter.

Dissolved Oxygen

Dissolved oxygen (DO) is also a useful measurement for determining the potential treatment options for an acid source. This analysis must be conducted in the field since the DO value will change quickly in a sample container. For acid drainage characterization purposes, the DO test is usually conducted on acid drainage seeps or springs, with the sample collected as close as possible to where the water comes out of the ground. This measurement is very important in deciding on and designing appropriate chemical or passive treatment systems since some types of systems function only within a limited range of DO concentrations.

Oxidation–Reduction Potential

Oxidation–reduction potential (ORP; also known as redox potential) of water is a measure of electron activity and is an indicator of the relative tendency of a biogeochemical system to accept or transfer electrons. ORP is the electric potential required to transfer electrons from one compound or element (the oxidant) to another compound (the reductant). It is also used as a qualitative measure of the state of oxidation in water treatment systems. Reduction potential is measured in volts or millivolts. Redox potential is a measure (in volts) of the affinity of a substance for electrons. This value for each substance is compared to that for hydrogen, which is set arbitrarily at zero. ORP meters are used in the field and values near −300 mV indicate highly reducing environments, or the ability to furnish electrons. Values from+100 to +300 mV indicate highly oxidizing environments, or the ability to accept electrons. Acid rock generation occurs in oxidizing environments as the pyrite is oxidized, forming sulfuric acid.

In electrochemistry, the standard-state potential of an oxidation–reduction reaction expressed in millivolts typically uses hydrogen reference electrodes as found in a laboratory. However, in the field, ORP instruments use the more portable and available platinum reference electrodes. Consequently, ORP measurements collected in the field are not the same as Eh measurements but can be corrected somewhat using Eh and ORP equations (Suthersan and Payne, 2005). Although ORP lacks a precise theoretical definition, the ORP measurements can provide general trends in redox activity, but many researchers have noted the challenges of obtaining reliable field ORP data. The ORP values can be combined with other parameters and aid in the overall interpretation of the redox of an aqueous environment.

Eh, typically measured in the laboratory and not in the field, shows the activity of electrons and is the potential of a platinum electrode measured in a water sample and corrected to a standard hydrogen reference electrode. Unfortunately, many researchers in the 1960s and 1970s noted that Eh values measured rarely correspond to Eh values calculated by the Nernst equation and aqueous concentrations of various redox couples for a variety of reasons, including poisoning of the platinum electrodes, lack of electrochemical equilibrium in natural systems, lack of internal equilibrium, and the consequent measurements of mixed potentials as summarized by Walton-Day et al. (1990) and Westall (2000).

Nordstrom (2000) noted that redox potential measurements with platinum electrodes work to estimate Fe(II)–Fe(III) activity ratios or sulfide activities when the concentrations are greater than about 10^{-5} M. One of the best ways to determine redox conditions of water is to analyze the sample for those redox species of special concern. There are several examples of the same water containing two or more of the following constituents: O_2, Fe(II), Fe(III), N_2, NO_3, NH_3, H_2S, SO_4, CH_4, CO_2, and H_2. In complicated cases where there are conflicting redox conditions in the same stream water sample, more detailed geochemical analyses of all major ions, redox pairs, trace elements, and selected isotopes should be performed and the geochemical data analyzed and compared with laboratory measurements and appropriate empirical formulas.

Salinity

Salinity is the percentage of salt in water. Salinity and saltwater specific gravity are especially useful when evaluating acid drainage from acid sulfate soils in coastal zones.

Saltwater Specific Gravity

Saltwater specific gravity indicates the density of water, whereas salinity refers to the actual weight of the salts.

Temperature

Temperature is important for many of the parameters, such as pH, because pH must be corrected for variations in temperature from 25°C. Several scales are used to measure temperature, the most common being Celsius (°C) and Fahrenheit (°F).

Total Dissolved Solids

Total dissolved solids (TDS) is all material that passes the standard glass river filter (a 2-µm filter); now called *total filterable residue*. TDS provides a qualitative measure of dissolved ions but does not tell us the types and ion relationships. The TDS concentration is not a health hazard by itself but has been linked as an indicator of the general quality of the water.

Turbidity

Turbidity is a cloudy condition in water due to suspended silt and clay or organic matter and is a measure of the quantity of the suspended solids or total suspended solids (TSS). Turbidity is measured in the field or in the laboratory in nephelometric turbidity units (NTU).

Acidity and Alkalinity

Alkalinity and acidity, related to pH, are important parameters for acid drainage studies but are usually

determined in the laboratory or using field kits with specific reagents and titration procedures.

Acidity

Acidity is a measure of the amount of base needed to neutralize an acid in a solution. It differs from pH in that pH is an expression of intensity, whereas acidity is a measure of amount. Two water samples can have the same pH but have very different acidity values. For example, acid rain has a relatively low pH (4.3), but the acidity concentration is low. It does not take much alkaline or basic material to neutralize the acidity in acid rain, due to a low concentration of the acid. Some acid drainage sites can have a similarly low pH but have high acidity concentration values. It is important to know the acidity concentration of an acid drainage site, since this will affect the type of treatment system, if needed, that may be designed to neutralize the acid.

Acidity field kits are available, and many use a simple titration process that works well as long as the value of the water being analyzed falls within the range of the kit. The titration kit measures field acidity by adding drops of a basic solution of known strength to the water sample. The amount of base (the number of drops) needed to reach an endpoint is a measure of the acidity. If a large amount of base must be added, the sample has a high acidity. It is also important to have the acidity measured in a laboratory since a more accurate and precise reading can be made in the laboratory than with a field kit. Since acid drainage is very unstable water, it is important to get the water samples to the laboratory quickly for acidity measurements or to perform the procedure in the field.

Alkalinity

Alkalinity is essentially the opposite of acidity and is a measure of a material's ability to neutralize acids. Similar to acidity measurement, alkalinity is commonly measured by titrating, but with an acid instead of a base. The more acid that needs to be added during the test, the higher the alkalinity. Alkalinity tests are done only on water that has a pH of 4.5 or greater. Below 4.5, no measurable alkalinity will be present in the water.

Screening Using Field Kits

As pH decreases during the acid generation process, many heavy metals become soluble and dissolve into water. Therefore, acid drainage is frequently associated with elevated levels of aluminum and iron as well as arsenic, cadmium, copper, lead, manganese, mercury, and zinc. Dissolved metals can be evaluated in the field or in the laboratory using a variety of water test kits. For acid drainage studies, to save time and lower fixed laboratory costs, field screening using semiquantitative and quantitative testing methods allows for a rapid assessment of water conditions at dozens or even hundreds of spot locations. Detailed field maps and even global positioning system (GPS) equipment can aid in establishing accurate locations of samples. Photos with scale markers enhance field documentation. Soil testing for various parameters, including pH and some dissolved metals, may be possible, and test kit manufacturers can provide details of the procedures for specific parameters. Field kits come in three main types: test strips, colorimetric methods, and titration methods.

Test Strips

For basic, rapid inexpensive screening in the field and spot testing for preliminary acid drainage studies, test strips can be used in water to analyze semiquantitatively for pH, chloride, and alkalinity and dissolved iron, arsenic, and copper. The test strips are dipped into water and the length of the color

change is compared to the values on a printed scale. The strips come in different ranges, depending on the expected concentration of the target parameter. The arsenic test strips from one manufacturer, for example, can measure below 10 parts per billion (ppb) of arsenic and come in two ranges: 0 to 500 ppb for the low range and 0 to 4000 ppb for the high range. Field dilution of the sample with deionized water can be used when sample concentrations in the field exceed the target range of the test strips.

Colorimetric Methods

A variety of methods exist using color changes of a sample compared to known colors associated with specific concentrations for a target parameter. Colorimetric methods can be used to quantitatively evaluate total iron and iron(II), chromium, copper, manganese, molybdenum, dissolved oxygen, and pH. For soluble iron measurements, the iron(II) or ferrous iron concentration is subtracted from the total iron concentration to provide the iron(III) or ferric iron concentration. Measurement accuracy for visual colorimetric methods is probably about ±10%. Color cube kits are the least expensive visual colorimetric method. They use a transparent plastic mixing cell for the sample and reagent(s) and an adjacent calibrated, stepped color comparator. The concentration is determined by comparing the calibration chart color visually with the color of the reacted sample. Color wheels use the same reaction chemistry as that of color cubes but use a continuous plastic color wheel to compare the reacted sample color with the color gradations on the color wheel (e.g., red for iron) from clear to opaque, reflecting low to high concentrations, respectively. Instrument-based colorimetric kits provide the higher accuracy and repeatability of digital readings as compared to the visual estimate of concentrations used by the color cube and color wheel kits. The same packets of premeasured reactants can be used for all the colorimetric methods, although the instrument costs are higher than those for color cube and color wheel kits.

Titration Methods

Two titration methods have been developed for use in acid drainage studies. The parameters include acidity, alkalinity, chloride, chromium, dissolved oxygen, and salinity. Titration, a quantitative method, can be slightly more accurate than visual colorimetric methods. In this procedure, the reactant is dropped into the sample container until a certain color is reached. In the drop-count method, the number of drops from a handheld dropper are counted to determine concentrations in the sample. A more accurate, expensive, and repeatable field titration method uses a digital titrator kit in which the results are comparable to buret titration.

Laboratory Confirmation Samples

Field validation and confirmation of field screening methods are generally carried out using a fixed laboratory with standard analytical methods and documented protocols. The use of specific laboratory methods will depend on the site history, regulatory data requirements, site-specific characteristics, and permit requirements as well as the required accuracy, precision, and laboratory reporting limits of the specific analytical methods.

Flow Measurements

Stream flow or *discharge* is a measure of water quantity. It is a measure of the volume of water moving past a fixed point on the stream or river over a given period of time. The factors involved in determining stream flow are the width and depth of the stream and the rate of water movement. Water flow is commonly measured in units such as cubic feet per second or gallons per minute in the United States and

in liters or cubic meters per unit time for the rest of the world.

Flow measurement is a critical component of characterizing streams for acid drainage. Accurate flow measurements provide information on the proportional effects that acid drainage sources have on the larger receiving streams or rivers. A large flow of low-pH water from a spring or hillside seep into a small stream will obviously have a more negative effect and a larger impact than will a small flow of equally acidic water into a large stream. It is especially important to measure the flow of acid drainage seeps and small acid drainage–affected tributaries because these water sources are most likely to be targeted for remediation projects such as passive treatment systems. It is especially important to get good approximations of typical low and high flows so that a good estimate of typical seasonal variations can be established. Because stream flow varies widely during the year, it is important to measure flow at the same site at different times of the year. In field areas having four seasons, flow data should be collected monthly or, at a minimum, quarterly. In locations with only two seasons (wet and dry), such as the American southwestern states of California, Arizona, New Mexico, and Nevada, for example, biannual sampling may be more appropriate.

Measuring Water Flow

As part of many acid mine drainage studies associated with streams, water flow measurements are frequently collected in the field. Descriptions of the instruments and methods used follow.

Bucket and Stopwatch Method

The simplest way to measure volumetric flow of seeps and small streams is to use the bucket and stopwatch method (Figure 9.3). This method uses a bucket of known volume and a stopwatch. The stopwatch is started when the flow starts and is stopped when the bucket overflows. The volume of water is divided by the time (usually, seconds or minutes) to calculate the flow (Skousen and Mains, 1997). It is important to channel all the flow into a pipe or structure and to capture all of it in the bucket. The procedure requires placing the bucket under the flow to collect the water and accurately measuring the time that it takes for the water to fill the bucket. Based on the size of the bucket and the amount of time needed to fill it, a good estimate of the flow can be made. Alternatively, the flow can be captured for a specific period of time and then the amount of water in the bucket measured. The procedure should be repeated several times to get an accurate measurement by averaging the results. This method is an “off-line” method, since the measurement cannot be made without interrupting the normal water flow.

FIGURE 9.3 Using the simple, but effective bucket and stopwatch method to estimate water flow.

Weir and Flume Method

Other methods to measure flow are more time consuming and expensive. Weirs and flumes are structures that are placed semipermanently in a stream. V-notch weirs can have either a 30°, 60°, or 90° notched angle. Flumes cause a constriction in the water flow. The height of the water flowing through the weir or the flume is measured, and if the width of the flume or the angle of the notch in a weir is known, the water flow can be calculated. Examples are provided later.

Water Flowmeter Method

For larger streams and rivers, the use of some type of water flowmeter which measures stream current velocity is necessary to estimate flow. In this method, the stream is divided into segments along a straight line from bank to bank perpendicular to the current. A cross-sectional area (width multiplied by depth) is measured for each segment. Then, using a flowmeter, the current velocity at a specified depth in the stream segment is measured. This allows for an estimate of flow in each segment. The estimates for each segment can then be added to obtain an overall estimate of the total stream flow. This method is not particularly accurate, but it is the best method available for rivers and larger streams. An example is provided later.

Stream flow data are an important aspect of accurate hydrologic characterization. The U.S. Geological

Survey's Hydrologic Instrumentation Facility has tested and evaluated current meters over a number of years (Fulford et al., 1993, 1994; Fulford, 2001). Although the U.S. Geological Survey (USGS) conducted water flow tests on some of the equipment described in these earlier papers, technical changes and improvements in these meters prompted the USGS to retest and reevaluate the inexpensive field instruments currently available (Thibodeaux, 2007). Five meters were evaluated: two standard USGS waterflow meters: Price-type AA meter and pygmy meter; two horizontal-axis meters: Global Water Flow Probe and the Swoffer (2- and 3-in. propeller models); and the advanced FlowTracker 2D ADV (acoustic Doppler velocimeter) (Figure 9.4).

FIGURE 9.4 The USGS conducted an evaluation of current meters to estimate stream velocity. (a) From top clockwise: Global Water Flow Probe FP101, SonTek/YSI FlowTracker 2D handheld ADV, Swoffer 3-in. prop, and Swoffer 2-in. propeller. (After Thibodeaux, 2007.) (b) USGS Price type AA (left) and pygmy. (After Thibodeaux, 2007.) (c) Numerous brands of meters are available to measure pH, conductivity, and temperature. Some more expensive meters also measure dissolved oxygen and reduction–oxidation potential (redox) to better understand water geochemistry, which is critical for understanding acid drainage. (Courtesy of J.G. Skousen.) (d) Several manufacturers offer simple acidity and other titration field kits, which are inexpensive and useful for acid drainage studies. (Courtesy of J.G. Skousen.)

These five meters were tested in the USGS's Hydraulic Laboratory's National Institute of Standards and Technology (NIST) traceable towing tank and tilting flume facilities. The test procedures are consistent with earlier USGS flowmeter studies and have been described by Thibodeaux (2007). Results presented show that the inexpensive horizontal-axis mechanical current meters did not meet their stated accuracy specifications from the manufacturers, whereas the handheld 2D ADV (FlowTracker) and the standard

USGS meters (AA and pygmy meters) did meet their stated accuracy specifications. Data collection is an important but sometimes overlooked part of evaluating acid drainage, and documenting observations and collecting accurate field information provide better technical results (Figure 9.5).

FIGURE 9.5 Collecting water flow data in the stream with a current meter. (Courtesy of J. Skousen.)

Collection and Storage of Water Samples

To confirm measurements collected in the field, a minimum of two water samples are required to evaluate acid drainage in a stream or water body. The allowable hold time is the time in which the sample must be analyzed to be legally valid. Hold times for the various analyses vary considerably. Published laboratory method descriptions usually specify the hold times. For the first water sample:

- pH (15-min hold time; usually performed in the field)
- Electrical conductivity (28-day hold time)
- Alkalinity (14-day hold time)
- Sulfate (28-day hold time)
- Other anions (28-day hold time)

For the second water sample:

- Metals analyses (typically, a 28-day hold time)

The first water sample is collected in an inert high-density polyethylene plastic container and transported to the laboratory in a refrigerated environment. This sample does not have to be filtered, but care should be taken when collecting the sample to ensure that visible sediments or particles are not collected with the water. If sediment or small particles can be seen in the sample, discard it and take another. If the water is cloudy and sediments cannot be avoided, the water should be filtered during collection. This sample will not have acid added to it. To conduct the laboratory analyses, about 250 mL (about a quart) to 500 mL (about a half gallon) of water is needed.

The second water sample is used for metal analysis (preserved in the field; 180-day hold time, except mercury, which is 28 days; nonpreserved samples in field: 24-hour hold time) and is also commonly collected in an inert high-density polyethylene plastic container and transported to the laboratory in a refrigerated environment. To get an accurate measurement of the amount of dissolved metals in the water, the water must be filtered, typically in the field, with disposable filters. Filtering water removes all the fine suspended particles, such as clays (also called soil colloids). If the suspended particles are not removed, these particles, containing iron, aluminum, and other metals, become dissolved when acid is added. This results in overestimating the dissolved metal content of the water. If filtering is not done, it is critical to collect a clear water sample without suspended particles. If the filtering occurs in the field, a few drops of nitric acid can be added in the field to put the metals in the water sample into solution; otherwise, the acid will be placed into the water sample in the laboratory. Acidifying the sample preserves it, keeps the metals in solution, and prevents the metals from adsorbing or adhering to the side of the container or precipitating, which would cause an underestimation of the metal content. Personal protective equipment such as goggles for eye protection, and chemically resistant gloves to protect skin should be used when adding the concentrated acid to the sample. (Always add the concentrated acid to the water, not the water to the acid.) The amount of water collected for this filtered and acidified sample can be much smaller than the first sample, but not less than 50 mL.

Legally Valid Samples

To be valid scientific and legal samples, groundwater samples for acid drainage should be collected in accordance with standard field protocols and submitted to a state or other regulatory agency–certified analytical laboratory. Sample preservation or filtering requirements may apply. The sample container labels should include sample number, sample date and time, sampler name, sample location, and analyses. Each water sample container should be labeled, documented on a chain-of-custody form, and placed in a refrigerated environment for transport to the central laboratory. For cases overseen by regulatory agencies, professional oversight of the project by a licensed engineer or geologist will probably apply. The chain-of-custody form is filled out in the field and lists each sampling container, the name of the sampler, the time and date the samples were collected, preservatives if added in the field, and laboratory procedures requested. The chain-of-custody form documents the chronological custody, control, transfer, analysis, and disposition of the sample and is signed by the sampler and all persons who have had custody of the samples until they arrive at the laboratory. A chain-of-custody form must be presented with the laboratory analytical report if the sample results are to be legally valid.

Stream Calculations for Acid Load

Once accurate flows have been obtained and acid concentrations have been determined in the laboratory, an estimate of the acid load can be calculated. The acid load is calculated by multiplying the flow in gallons per minute by the acidity (mg/L as $CaCO_3$), then multiplying by 0.0022. The value of 0.0022 is a

conversion factor that translates the flow and acid concentration to an amount of acid over a specified time. In this case, the conversion factor gives the acid load value in tons of acid per year. This value is used, along with other factors, to design a chemical or passive treatment system for that particular water source. Costs associated with the treatment can also be evaluated.

Flow Measurement Examples and Exercises

Bucket and Stopwatch Method

This method is fast, easy, and well suited for flows less than 100 gal/min (see Figure 9.3). All the water must be channeled from a point source through a pipe or over a fall. Usually, a 1- or 5-gal bucket and stopwatch are used to capture all the water for a specified time (usually, 5 to 30 s) at the sample point. It helps to have a calibrated bucket or a way to measure the amount of water in the bucket. Accuracy depends on the ability to channel all of the water into the container and to measure the elapsed time. When collecting water (gallons) for the following amounts of time:

$$\text{water collected in 5 s} \times 12 = \text{flow}$$
$$\text{water collected in 6 s} \times 10 = \text{flow}$$
$$\text{water collected in 10 s} \times 6 = \text{flow}$$
$$\text{water collected in 15 s} \times 4 = \text{flow}$$
$$\text{water collected in 30 s} \times 2 = \text{flow}$$

the flow (gal/min) can be calculated as follows: 3 gal of water is collected in a bucket over 5 s × the conversion factor of 12 = a flow of 36 gal/min. The conversions (12, 10, 6, etc.) are calculated by dividing 60 s by the amount of time the water was collected. For example, 60 s divided by 5 equals 12.

Example Water was allowed to flow into a bucket for exactly 15 s. The amount of water in the bucket was 1.25 gal. What was the flow?

$$1.25 \text{ gal} \times 60/15 \text{ (or 4)} = 5 \text{ gal/min}$$

Rather than collecting water for a specific period of time and then measuring the volume of water, a variation of this method is to time how long it takes to fill the bucket completely. The flow can be determined using the following formula:

$$60 \div \text{the time in seconds} \times \text{volume of the bucket} = \text{flow (gal/min)}$$

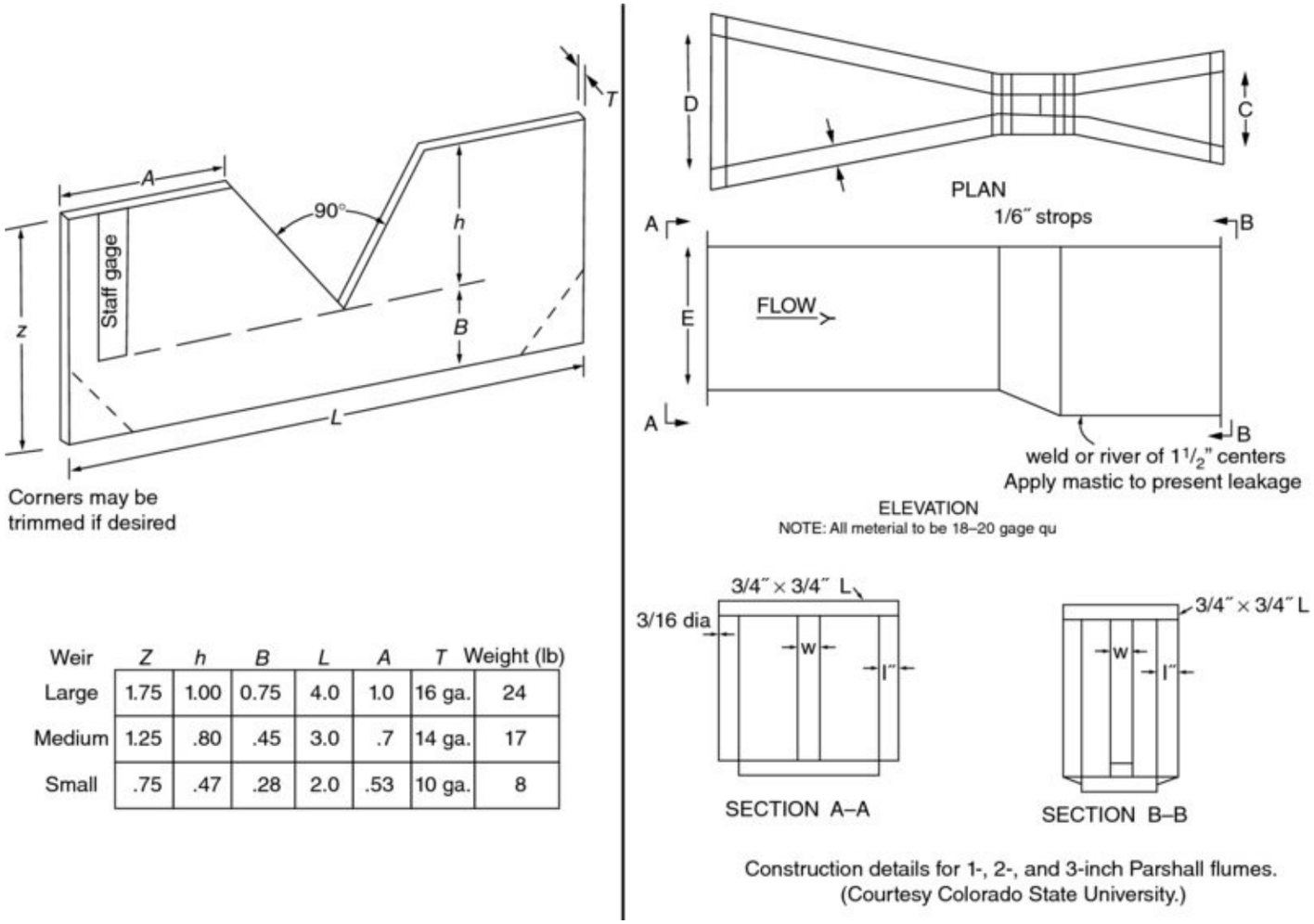
Example It took 47 s to fill a 5-gal bucket completely. What is the flow?

$$60/47 \times 5\text{gal} = 6.4 \text{ gal/min}$$

Weirs and Flumes

Weirs and flumes are devices or structures that cause water to flow in a specified manner. The flow is measured by the height of water flowing through the device. These methods work well for flows from 100 to 5000 gal/min. Design elements of weirs and flumes are shown in Figure 9.6. An actual weir and flume are shown in Figure 9.7 and 9.8, respectively. Complete damming of the stream or seep to divert all the

water through a weir or flume is required for this type of flow measurement. Normally, low flows or small channels can be dammed fairly easily. These flow measurements are accurate if the weir or flume was constructed properly, installed correctly, and calibrated. Standard tables or formulas can be used to determine flow. A fall of 3 to 6 in. is necessary once water passes through a weir, but a fall after the device is not needed for a flume. A calculator that can handle numerical exponents is needed to do some of the exercises that follow: Also note that while initial calculations yield flow measurements in cubic feet per second, for small flows the preferred final units are typically gallons per minute. The ft^3/s value multiplied by 449 gives the gal/min value.



Weir	Z	h	B	L	A	T	Weight (lb)
Large	1.75	1.00	0.75	4.0	1.0	16 ga.	24
Medium	1.25	.80	.45	3.0	.7	14 ga.	17
Small	.75	.47	.28	2.0	.53	10 ga.	8

Construction details for 1-, 2-, and 3-inch Parshall flumes.
(Courtesy Colorado State University.)

FIGURE 9.6 On the left, portable weir plate dimensions; on the right, a design for a Parshall flume.

FIGURE 9.7 V-notch weir inserted into a stream to measure flow.

FIGURE 9.8 Parshall flume inserted into a stream to measure flow in operation. (Courtesy of J.G. Skousen.)

V-Notch Weirs

Ninety-degree weirs are the most common. There must be sufficient room upstream of the weir for the damming of water. The weir must be sealed completely so that no water goes around or under the weir. All water must flow through the weir. The top of the weir must be level and the sides vertical. The water level (head) must reach a steady level upstream of the weir:

$$\text{flow through a } 90^\circ \text{ V-notch weir} = Q = 2.5H^{5/2}$$

where Q is the flow (ft^3/s) and H is the height of the water in the weir (ft).

Example What is the flow (gal/min) through a 90° V-notch weir if the height of water in the weir is 4 in. (0.33 ft)?

$$0.33^{5/2} = 0.33^{2.5} = 0.063 \times 2.5$$
$$= 0.156 \text{ ft}^3/\text{s} \times 449 \text{ gal}/(\text{ft}^3/\text{s}) = 70.2 \text{ gal/min}$$

Exercise What is the flow through a 90° V-notch weir if the height of water is 1 in. (0.0833 ft)? How about 6 in. or 10 in.?

(*Answers:* 1 in. = 2.3 gal/min; 6 in. = 198 gal/min; 10 in. = 712 gal/min.)

Flumes

Flumes channel flow through a constriction, causing an increase in velocity. The most common are Parshall flumes with 3- or 6-in. throat widths. The flume must be level, but damming the stream is not required:

$$\text{flow through flume} = Q = 4Wh^{1.522W\ \exp(0.026)}$$

where Q is the flow (ft^3/s), W is the throat width (ft), and h is the upper head or height of water in the flume (ft).

Example What is the calculated flow through a Parshall flume with a throat width of 2.0 ft at the maximum free-flow head (height) of 1.5 ft?

$$\begin{aligned} 2.0^{0.026} &= 1.0182 \times 1.522 = 1.55 \\ 1.5^{1.55} &= 1.8747 \times 2.0 \times 4 \\ &= 15\ ft^3/s \times 449\ (ft^3/s)/(gal/min) = 6734\ gal/min \end{aligned}$$

Exercises What is the flow through a Parshall flume with a throat width of 2.0 ft at the upper head of 2.5 ft? What is the flow through a Parshall flume with a throat width of 0.25 ft (3 in.) at the upper head of 0.167 ft (2 in.)?

(*Answers:* 14,864 gal/min and 259 gal/min.)

Practical Water Flow Measurements

Water flowmeters are used to measure the velocity of the stream current, which is used together with width and depth measurements to approximate stream flow. The meter method involves summing the products of cross-sectional areas of stream segments and their average velocities. Depending on the size of the stream, 10 to 30 subsections (usually, 1 ft in width) are delineated with a tape measure, and the depth and average velocity of each subsection are measured.

In streams with depths of less than 5 ft, average velocity may be taken as a single velocity with the meter held at a point below the water surface that is 0.6 (or 60%) of the distance from the surface to the stream bottom. For example, if a subsection of a stream is 2 ft deep, the average velocity should be measured 1.2 ft down from the surface (or 0.8 ft up from bottom). In subsections deeper than 5 ft, the velocity is measured at 20% and 80% from the surface and averaged to obtain the average velocity for that subsection. For these deeper streams, the meter is usually lowered from a bridge. Many mountain streams are shallow enough for a person to wade into to take measurements. The person should be careful to stand downstream and not cause the water to back up from where he or she is standing to influence the velocity of the water. Care should be taken when wading in deeper streams, especially those with swifter currents.

Example A stream is 10 ft wide. The stream is divided into 10 subsections, each of 1 ft width. The average depths of each subsection from the left bank to the right bank are as follows: 6, 9, 11, 13, 15, 14, 12, 8, 7, and 5 in. The velocity at each of these points was 0.1, 0.3, 0.4, 0.8, 1.2, 1.4, 0.9, 0.5, 0.3, and 0.1 ft/s, respectively. What is the flow or discharge of the stream in ft^3/s and gal/min?

The depth measurements must be converted to feet. To get the cross-sectional areas of each subsection, the average depth must be multiplied by the width of the subsection, which is 1 ft in this example. The cross-sectional area of each subsection is multiplied by the average velocity of each subsection,

determined by using the meter. The calculations are given in Table 9.1.

Table 9.1 Depth and Width Data for Flow Calculation Exercise

					(Depth×Width)				
Depth	**Depth**	**×**	**Width**	**=**	**Cross-Sectional Area**	**×**	**Velocity**	**=**	**Flow**
(in.)	**(ft)**		**(ft)**		**(ft^2)**		**(ft/s)**	**(ft^3/s)**	
6 in.×1 ft/12 in. =	0.50	×	1	=	0.50	×	0.1	=	0.050
9 in.×1 ft/12 in. =	0.75	×	1	=	0.75	×	0.3	=	0.225
11 in.×1 ft/12 in. =	0.92	×	1	=	0.92	×	0.4	=	0.368
13 in.×1 ft/12 in. =	1.08	×	1	=	1.08	×	0.8	=	0.864
15 in.×1 ft/12 in. =	1.25	×	1	=	1.25	×	1.2	=	1.50
14 in.×1 ft/12 in. =	1.17	×	1	=	1.17	×	1.4	=	1.64
12 in.×1 ft/12 in. =	1.00	×	1	=	1.00	×	0.9	=	0.900
8 in.×1 ft/12 in. =	0.67	×	1	=	0.67	×	0.5	=	0.335
7 in.×1 ft/12 in. =	0.58	×	1	=	0.58	×	0.3	=	0.174
5 in.×1 ft/12 in. =	0.42	×	1	=	0.42	×	0.1	=	0.042
					Total of all subsections			=	6.098 ft^3/s
					6.098 ft^3/s	×	449 (gal/min)/(ft^3/s)	=	2738 gal/min

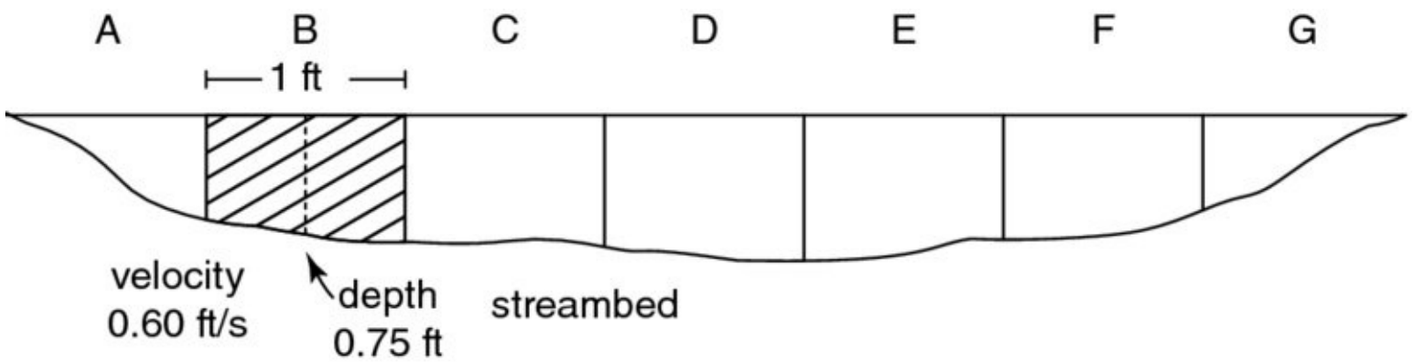


FIGURE 9.9 Stream cross section for flow estimation exercise.

Flow Estimation Exercise

This exercise uses the cross-sectional area shown in Figure 9.9:

Example A stream is 7 ft across. The stream is divided into 1-ft sections, A through G. Depth and flow velocity are measured in the middle of each section. Calculate the flow in this cross section of stream

using width×depth×velocity. Sum all the cross sections of the stream together to estimate the total flow (note that ft^3/s needs to be converted to gal/min). Data for this example are given in Table 9.2.

$$3.32\ ft^3/s \times 449\ gal/min = 1491\ gal/min$$

Here the conversion to 449 gal/min is

$$1\ ft^3/s = 7.48\ gal/s \times 60\ s/min = 449\ gal/min$$

Table 9.2 Flow Calculation for Stream Cross Section in Figure 9.9 with Depth, Width and Velocity Data.

	Section							Total (ft^3/s)
	A	**B**	**C**	**D**	**E**	**F**	**G**	
Width (ft)	1	1	1	1	1	1	1	
Depth (ft)	0.3	0.75	0.71	0.79	0.67	0.50	0.17	
Velocity (ft/s)	0.25	0.60	0.90	1.3	1.1	0.75	0.10	
Total	0.075	0.45	0.639	1.027	0.737	0.375	0.017	3.32

Exercises

1. A stream is 5 ft wide. The stream is divided into five subsections, each 1.0 ft in width. The average depths of each subsection from the left bank to the right bank are as follows: 3, 5, 9, 6, and 2 in. The velocities at each of these points, respectively, were 0.1, 0.3, 0.5, 0.4, and 0.2, all in ft/s. What is the flow or discharge of the stream in ft^3 and gal/min?

   Answer: The stream is 5 ft wide = (5) 1-ft-wide sections (A through E). Convert all depths in inches to feet.

	Section					Total (ft^3/s)
	A	**B**	**C**	**D**	**E**	
Width (ft)	1	1	1	1	1	
Depth (ft)	0.25	0.42	0.75	0.50	0.17	
Velocity (ft/s)	0.1	0.3	0.5	0.4	0.2	
Total (ft^3/s flow)	0.025	0.126	0.375	0.200	0.034	0.760 ft^3/s (just add up)

   The flow in ft^3/s = 0.760 ft^3/s. The total flow in gal/ min = ft/s×conversion factor (449 gal/min = 1 ft^3/s). 760 ft^3/s×7.48 gal/s×60 s/min = 341 gal/min.

2. (a) What is an inexpensive method to collect 100 pH readings in the field? Explain your answer.

   Answer: A calibrated pH meter is reasonably accurate. Low-cost field methods include using pH paper, and acid–base chemistry titrations can also be used.

   (b) How would you follow up or confirm your initial findings with more exact information?

   Answer: Water samples that have been collected are ideally representative of the field conditions and are best if the results are reproducible so that another sample collected at the same location under

virtually identical conditions would yield similar results. Collecting duplicate water samples and analyzing both samples to see if the water samples have nearly identical pH results provides a higher level of field confidence. Field pH confirmation can be obtained by collecting water samples from the field and submitting the samples under chain-of-custody procedures to a state-certified laboratory and analyzing for the pH of the water under laboratory conditions using an electrometric instrument according to U.S. EPA Method 150.1, which requires instrument calibrations and documentation.

3. What is the flow (in gal/min) through a 90° V-notch weir if the height of water in the weir is 6 in. (0.50 ft)?

   Answer: Recall that flow through a 90° V-notch weir = $Q = 2.5H^{5/2}$, where Q = flow (ft^3/s) and H = height of water in the weir (ft). Convert ft^3/s to gal/min: 0.442 $ft^3/s \times 449$ $ft^3/s/gal/min$ = 198 gal/min.

4. (a) Is it is possible to have a negative pH?

   Answer: Yes.

   (b) Explain how a negative pH is possible?

   Answer: Although the pH for most aqueous solutions and natural waters is often presented on a scale from 0 to 14 and common household liquids lie within the range, the scale is not fully accurate, especially when discussing acid drainage. Pure water at 25°C is completely neutral at a pH of 7.0. The usual general chemistry text definition of pH is $-\log[H^+]$ (the negative logarithm of the hydrogen-ion molarity), so that if the molarity of hydrogen ions is greater than 1.0, the pH will have a negative value. As an example, a 12 M HCl solution would have a pH of $-\log(12) = -1.08$. A better definition of pH is $= -\log a_{H^+}$ (the negative logarithm of the hydrogen-ion activity). A detailed technical description of pH is included in an article by Nordstrom et al. (2000). In this article the authors describe extremely acidic mine waters with pH values as low as −3.6, total dissolved metals concentrations as high as 200 g/L, and sulfate concentrations as high as 760 g/L at the Richmond mine at Iron Mountain, California.

   Reference: Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., and Blowes, D.L., 2000. Negative pH and extremely acidic mine waters from Iron Mountain, California. Environmental Science and Technology, vol. 34, no. 2, pp. 254–258.

5. Why is it best to filter water samples that will be analyzed for metals?

   Answer: Metals can attach to soil colloids that are in suspension in a water sample. Frequently, samples with high turbidity have high suspended solids and floating colloidal material. Removing the metals that are attached to colloids and other particles provides a more accurate concentration of metals dissolved in a water sample.

6. (a) If some seeps are seasonal, is it worth investigating the potential acid drainage seeps at different times of the year to verify flow, pH, and other geochemical parameters?

   Answer: To obtain accurate site information and acid drainage potential, the full hydrologic cycle must be understood, and whether the sulfur-rich zones are above the water table with oxidizing conditions or completely saturated throughout the year, which can lead to reducing conditions. Aerobic conditions that allow for oxygen in the soil pore spaces or some level of dissolved oxygen in the shallow groundwater will encourage aerobic microbial communities, which will favor the generation of acid drainage. Reducing conditions will encourage facultative and anaerobic microbial communities which are not associated with iron- and sulfur-oxidizing processes.

(b) Is there likely to be much variation in these parameters over a period of a year?

Answer: There could easily be major changes in surface or groundwater elevation over the course of a year. As surface or groundwater elevations change, depending on where the boundary between the saturated zone and the unsaturated zones occurs, the geochemistry can change significantly, and the stability of pyrite-rich rocks, sediments, or soils, the source of most acid drainage, can be greatly affected.

(c) What is the minimum number of inspections per hydrologic cycle that would be needed in coastal California if there is usually one wet and one dry season over a period of 1 year?

Answer: A minimum of two inspections would be required per year. However, additional inspections early in a project allow for documentation of the variations in temperature, precipitation, groundwater or water elevations, and other factors that might affect acid drainage.

References and Suggested Reading

Fulford, J.M., 2001. Accuracy and consistency of water-current meters. Journal of the American Water Resources Association, vol. 37, no. 5, pp. 1215–1224.

Fulford, J.M., Thibodeaux, K.G., and Kaehrle, W.R., 1993. Repeatability and oblique flow response characteristics of current meters. In: Hydraulic Engineering ’93: Proceedings of Conference, Hydraulic Division, July 25–30. American Society of Civil Engineers, New York, pp. 1452–1457.

Fulford, J.M., Thibodeaux, K.G., and Kaehrle, W.R., 1994. Comparison of current meters used for stream gaging. In: Fundamentals and Advancements in Hydraulic Measurements and Experimentation. Proceedings of Symposium, Hydraulic Division, August 1–5. American Society of Civil Engineers, New York, pp. 376–385.

Nordstrom, D.K., 2000. Aqueous redox chemistry and the behavior of iron in acid mine waters. In: Proceedings of the Workshop on Monitoring Oxidation–Reduction Processes for Ground-water Restoration, Dallas, TX, April 25–27, R.T. Wilkin, R.D. Ludwig, and R.G. Ford, eds. EPA/600/R-02/002. U.S. Environmental Protection Agency, Cincinnati, OH, pp. 43–47.

Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., and Blowes, D.W., 2000. Negative pH and extremely acidic mine waters from Iron Mountain, California. Environmental Science and Technology, vol. 34, no. 2, pp. 254–258.

Skousen, J., and Mains, C., 1997. Watershed Characterization Handbook for Streams Impacted by Acid Mine Drainage: You Can't Judge a Stream by Its Color. West Virginia University, Extension Service, Morgantown, WV, 37 pp.

Suthersan, S.S., and Payne, F.C., 2005. In Situ Remediation Engineering. CRC Press, Boca Raton, FL, 511 pp.

Terrel, C.R., and Perfetti, P.B., 1989. Water Quality Indicators Guide: Surface Water. SCS-TP-161. U.S. Soil Conservation Service, Washington, DC, 128 pp.

Thibodeaux, K., 2007. Testing and evaluation of inexpensive horizontal-axis mechanical current meters. In: The Role of Irrigation and Drainage in a Sustainable Future, Proceedings of the 2007 U.S. Committee on Irrigation and Drainage 4th International Conference on Irrigation and Drainage, Sacramento, CA,

October 3–6, pp. 1295–1309.

U.S. Environmental Protection Agency, 1997. Volunteer Stream Monitoring: A Methods Manual. EPA 841-B-97-003. U.S. EPA, Office of Water, Washington, DC, 210 pp.

U.S. Forest Service, 2010. Stream Systems Technology Center, Stream Notes. http://stream.fs.fed.us/news/streamnt/jul02/jul_02_05.htm.

Walton-Day, K., Macalady, D.L., Brooks, M.H., and Tate, V.T., 1990. Field methods for measurement of ground water redox chemical parameters. Ground Water Monitoring Review, Fall, pp. 81–89.

Westall, J.C., 2000. Geochemical equilibrium and the interpretation of Eh. In: Workshop on Monitoring Oxidation–Reduction Processes for Ground-water Restoration, Workshop Summary, Dallas, TX, April 25–27, R.T. Wilkin, R.D. Ludwig, and R.G. Ford, eds. Office of Research and Development, U.S. Environmental Protection Agency, Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Ada, OK, pp. 21–24.

10
Overview of Soil and Groundwater Sampling Methods for Acid Drainage Studies

JAMES A. JACOBS

The objectives of evaluating environmental conditions associated with acid drainage, whether it is from pyrite-rich rocks from mining projects, ground disturbance during construction projects, or development in naturally occurring acid sulfate soils, require the collection of representative soil and groundwater samples. Depending on the planned depth of disturbance, soil, sediment, and rock samples for acid drainage projects will be collected within 30 ft of the ground surface and probably within the top 5 to 10 ft below the ground surface. Certain situations may require significantly deeper soil or groundwater samples, such as waste mine rock with a high sulfide content that has been placed in a deep surface mine pit.

Introduction

For mining operations and areas where rocks are broken into smaller fragments, such as in waste tailing piles, the soil sampling equipment may be as simple as hand augers. For greater depth and better sample production, direct-push technology rigs, cone penetrometer rigs, and small rotary hollow-stem auger or flight auger rigs may be appropriate, depending on the subsurface conditions, accessibility, time available, and project budget. Sometimes, backhoes and excavators are used to collect bucket samples from trenches or pits for acid drainage evaluation projects. For deeper or more cemented sediments and drilling into bedrock, mud rotary drilling rigs with diamond-core bits and other powerful drilling methods may be needed. The following is a summary of some of the sampling and drilling methods used in the field to evaluate acid drainage.

Field Study Methods

Excavator or Backhoe Samples

For shallow pit or trench sampling of soils or soft or poorly cemented sediments, an excavator can be used to a depth of about 20 to 30 ft below the ground surface. A backhoe can be used for trench or test pit sampling to a depth of about 15 to 20 ft below the ground surface. Test pits allow for detailed examination of subsurface soils and sediments. Shoring may be required for workers to go into test pits. The introduction of aerated surface waters and atmospheric oxygen into the anaerobic subsurface through pit or trench sampling may contribute to the start of acid generation, so the unintended consequences of field investigation activities should be anticipated carefully.

Drilling Techniques

A variety of drilling techniques have been developed and are used in the environmental field, some of which are applicable to acid drainage studies. The factors to determine the best drilling technique relate to accessibility, time, and cost of project, sediment type (consolidated rock or unconsolidated soils),

sample type (undisturbed vs. disturbed), and sample integrity. Unconsolidated deposits are drilled primarily using hollow-stem augering techniques, with an occasional use of cable-tool drilling techniques. For consolidated or semiconsolidated deposits, continuous wire-line or conventional rock coring techniques are commonly used.

Drilling techniques used in the environmental field include the use of labor-intensive hand augers for shallow depths and machine-operated solid-flight augers. Both of these techniques can have sample retrieval problems since samples can only be collected if the entire auger is removed prior to sampling . More detail regarding drilling techniques has been provided by Driscoll (1984), Testa (1994), Sisk (1981), and the California Department of Water Resources (1981, 1990). The drilling and sampling equipment may vary slightly but is generally available worldwide. The sampling procedures and drilling equipment described are used in the United States.

Manual Sampling Methods

The most basic of all soil sampling equipment is the manually operated slide hammer, with connector rod and soil sampling cup. This sampling method works well for a large number of surface and very shallow soil samples, which might be common in an acid drainage study. Handheld slide hammers, typically weighing 12 to 30 lb, are dropped approximately 12 to 24 in. onto steel extension rods. The soil sampler with retaining sample liner is connected to the leading edge of the extension rods. Some portable soil sampling systems have foot pedals attached to the rods which allow the operator to step down to push the soil sampler into the ground. The sampling depth can be increased using small handheld augers to drill down to the target depth. In soft soils, the maximum depth of manual sampling is approximately 10 to 15 ft; in hard to moderately hard soils, the depth of sampling is approximately 2 to 8 ft. Benefits for the manual sampling method are minimal setup time, low costs, and minimum disturbance of the site. The depth of sampling is the limiting factor in the manual sampling method, and the level of physical effort is high. The manual soil sampler cup is usually constructed of heat-treated stainless steel and ranges from about ½ to 2 in. in diameter and about 6 in. to 2 ft in length. Rotohammers or jackhammer attachments can make the manual sampling easier.

Direct-Push Technology Sampling

Small, highly maneuverable direct-push technology probes were developed in the late 1980s using an industrial jackhammer to drive the soil coring tools into the subsurface. Direct-push technology sampling tools work well with a variety of soils derived from ore bodies, which might be found in shallow soils in mining areas. The soils typically found in acid sulfate soil areas could easily be collected using direct-push technology samplers. These samplers have been used successfully in sensitive environments such as rivers and coastal environments, including wetlands, lagoons, estuaries, and bay settings, and for unconsolidated sediments, including clays, silts, sands, gravels, and mining or construction waste rock less than about 0.5 to 1 in. in diameter. The sampling tools are not designed to penetrate or sample dense lithologies or bedrock. Many probe rigs can drill angle borings from about 30° to 45° from vertical. Some rig manufacturers have enhanced the direct-push technology vibrating percussion hammers with sonic coring capabilities.

Cone Penetrometer Testing Method

Used in the geotechnical engineering industry for decades, cone penetrometer testing (CPT) rigs use the static weight of a vehicle to push sampling rods into the ground. CPT rigs use a 20-ton truck and are capable of sampling in soils to depths of 250 ft. CPT rigs typically push from the center of the truck, so

angle borings are not possible with this configuration. In addition to taking soil and water samples, CPT tooling includes probes equipped with transducers for measuring point penetration resistance and sleeve friction of the borehole. An empirical relationship exists between the physical strength measurements and soil types, and the data are used to develop soil classification logs for the layers penetrated.

Hollow-Stem Auger Drilling

A variety of different auger drilling techniques have been developed for the environmental and engineering industry and are used for acid drainage evaluation projects. The factors to determine the best auger drilling technique relate to accessibility, time and cost of project, sediment type (consolidated rock or unconsolidated soils), sample type (undisturbed vs. disturbed), and sample integrity. Unconsolidated deposits are drilled primarily using hollow-stem augering techniques, with an occasional use of cable-tool drilling techniques. For consolidated or semiconsolidated deposits, continuous wire-line or conventional rock-coring techniques are commonly used.

Continuous Coring Tube Method

In the continuous coring method of sampling, the borehole is advanced by pushing a 2- to 3-in.-diameter steel tube into the ground and withdrawing it at intervals to extrude a soil or sediment sample. Continuous coring tubes are sometimes referred to as Shelby tubes.

Continuous Flight Auger Drilling

Continuous flight auger drilling uses augers which are withdrawn at selected intervals to allow for soil sampling or in situ testing. This is a relatively economical means of drilling in clays and in sands above the water table. Samples are returned to the surface or may be collected after withdrawal of the auger flights, but they are very disturbed and may be cross-contaminated.

Rotary Drilling

Rotary drilling techniques include direct mud rotary, air rotary, air rotary with a casing driver, and dual-wall reverse circulation. Direct mud rotary drilling uses fluid that is pumped down through the bit at the end of the drill rods. Then it is circulated up the annular space back to the surface. The fluid at the surface is routed via a pipe or ditch to a sedimentation tank or pit, then to a suction pit where the fluid is recirculated back through the drill rods. Air rotary drilling is similar to that of direct mud rotary, except that air is used as a circulation medium instead of water. Although the air helps cool the bit, a small quantity of water or foaming surfactants is used to facilitate sampling. In unconsolidated deposits, direct mud or air rotary can be used, provided that a casing is driven as the drill bit is advanced. In dual-wall reverse circulation, the circulating medium (mud or air) is pumped downward between the outer casing and the inner drill pipe, out through the drill bit, then up the inside of the drill pipe.

Rotary drilling techniques are commonly limited to consolidated deposits of rocks and typically are not used in subsurface environmental studies, due to poor sampling capabilities. Sample integrity is questioned since the added water, mud, or surfactant may react chemically with the formation water. In addition, thin water-bearing zones are often missed. With mud rotary, the mud filter cake that develops along the borehole wall may adversely affect the permeability of the adjacent formation materials. With air rotary, dispersion of potentially hazardous and toxic particulates in the air during drilling is a concern. Air rotary drilling techniques are fast. Where the subsurface geology is relatively well characterized or a resistant stratum such as overlying basalt flows or conglomerate strata exists at shallow levels within the vadose zone and above the depth of concern, using an air rotary rig to drill to a predetermined depth

followed by another, more suitable drilling technique may be worth considering (Testa, 1994).

Wire-Line Coring Method

Wire-line core drilling produces cylindrically shaped cores. A rotary rig is used in conjunction with water, drilling mud, or air. The core diameter varies depending on bit size, manufacturer specifications, or standards supplied by the Diamond Core Drill Manufacturers Association. Core sizes generally range from about ¾ in. to greater than 6 in. Cutting is accomplished by drill bits located at the end of a rotating barrel or tube. The barrel gradually slides down into the annular opening. The core is then separated from the rest of the formation mass, and the barrel containing the core is retrieved.

Both single- and double-tube core barrels exist. In double-tube core barrels, the inner tube retains the core while the tube rotates. Double-tube core barrels are often used in unconsolidated formations, where sloughing may be a problem. Double-tube barrels may be of fixed or swivel type. The inner tube of the fixed type rotates with the outer tube. The purpose of the inner tube is to provide a shroud over incoming cores and to avoid washaway by high-pressure drilling fluid and also to carry the core catcher for catching the core upon withdrawal. The swivel type prohibits the inner tube from rotating. In both types, the inner tube is adjustable up or down within the outer tube to reduce or increase exposure of the incoming core to the erosive velocity of the drilling fluid.

Cable-Tool Drilling

Cable-tool drilling is the oldest drilling technique available and is not often used in the environmental field, as the technique is slow, noisy, and dusty. Nonetheless, cable-tool drilling may be used in mining areas with large buried cobbles and boulders. Other locations where cable-tool drilling rigs are used is in glacial environments containing large cobbles, as in the Pacific Northwest of the United States, and in young volcanic rocks such as in Hawaii. Cable-tool rigs, called percussion or spudder rigs, operate by repeatedly lifting and dropping the heavy string of drilling tools in the borehole, crushing larger cobbles and rocks into smaller fragments. During cable-tool drilling, the hole is continuously cased with an unperforated 8-in.-diameter steel casing with a drive shoe. The casing is attached on top by means of a rope socket to a cable that is suspended through a pulley from the mast of the drill rig. The process of driving the casing downward about 3 to 5 ft is followed by periodical bailing of broken rocks and accumulated soils from the bottom of the borehole. Water is needed to create a slurry at the bottom of the borehole. When formation water is not present, water is added to form a slurry. The addition of large volumes of water into the formation to create the slurry may degrade and compromise the quality of environmental samples.

Groundwater Monitoring with Well Points

Once the site acid generation investigation objectives have been met, small-diameter well points (0.5 to <2 in. in diameter) can be installed to monitor shallow groundwater, if needed. Direct-push technology well points are typically installed without filter packs. However, robust filter pack materials specifically designed for rapid customization of direct-push technology well points have recently become available. Direct-push technology well points or piezometers with up to about a 1.0-in. inside casing diameter can been used for groundwater sampling and to gauge groundwater elevations at acid drainage sites. Well points can be designed and installed with premade sand filter packs. The well points are sealed with bentonite and cement as in a normal monitoring well.

Well Installation Methods

The purpose of monitoring a well network is to define groundwater quality and movement and to accomplish specific study objects: A work plan and drilling permit application are frequently submitted to and approved by the lead regulatory agency prior to well installation. The borehole for a monitoring or extraction well is frequently drilled using a truck-mounted continuous flight hollow-stem auger drill rig. The borehole diameter for monitoring wells (not driven well points) is usually a minimum of 2 to 4 in. larger than the outside diameter of the well casing, in accordance with appropriate regulatory guidelines. A hollow-stem auger provides minimal interruption of drilling while permitting soil sampling at the desired intervals. All wells should be installed by licensed drillers.

Well materials for monitoring and extraction wells must be chemically compatible with the potential contaminants. Casing, both blank and screen sections, can be constructed of fiberglass-reinforced plastic, stainless steel, concrete, or thermoplastic which includes poly(vinyl chloride) (PVC), acrylonitrile–butadiene–styrene, and styrene–rubber. Based on cost, availability, and chemical compatibility, the most common casings and screens used for shallow drilling projects in the environmental field are made of PVC. Deeper wells are typically constructed of either heavier-gauge PVC or steel.

In Situ Remediation Systems

For remediation purposes, direct-push technology equipment, including both probe and CPT rigs, can provide a closely spaced liquid or grout delivery system for in situ remediation of soils and water affected by acid drainage. Monitoring wells, direct-push technology injection rods, and well points can be used for the delivery of in situ chemicals and grouts for treating acid drainage. The delivery ports can be used to inject: (1) chemical reducing agents; (2) biocides to kill sulfide-oxidizing bacteria; (3) liquid or grout carbon substrates for creating fermentable anaerobic subsurface environments to lower dissolved oxygen content in groundwater and create temporary reducing conditions; and (4) liquid or grout neutralizing agents on close spacing.

Even gas infusion using hollow-fiber membrane technologies can be used to change redox conditions or pH in 2-in.-diameter monitoring wells. Although gas, liquid, and grout injections are unlikely to fully treat the subsurface permanently, in situ applications may provide enough temporary treatment to prevent acid generation from starting during a planned mine or development project. In situ treatment could be planned for implementation during field operations to maintain anaerobic conditions within the shallow aquifers and keep reducing conditions for potential acid sulfate soils. Once the mining or development project is finished and the site disturbance has been completed, the use of alkaline or reducing treatment chemicals might be discontinued as the subsurface geochemistry reverts to neutral anaerobic conditions. In situ treatment requires detailed engineering design, bench testing, pilot testing, regulatory approval, and a significant monitoring program.

References and Suggested Reading

American Society for Testing and Materials, 1984. Standard Practice for Description and Identification of Soils: Visual-Manual Procedure. Method D2488–84. ASTM International, West Conshohocken, PA.

California Department of Water Resources, 1981. California Well Standards. Bulletin 74–81. DWR, Sacramento, CA.

California Department of Water Resources, 1990. California Well Standards. Bulletin 74–90. DWR, Sacramento, CA.

California Regional Water Quality Control Board, 1989. Leaking Underground Fuel Tank (LUFT) Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. RWQCB, Sacramento, CA.

California Regional Water Quality Control Board, 1990. Tri-regional Board Staff Recommendations for Preliminary Investigation and Evaluation of Underground Tank Sites. RWQCB, Sacramento, CA.

California Regional Water Quality Control Board, 2010. Leaking Underground Fuel Tank (LUFT) Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. RWQCB, Sacramento, CA.

Driscoll, F.G., 1986. Groundwater and Wells, 2nd ed., Johnson Filtration Systems, St. Paul, MN, pp. 268–339.

Isbell, R.F., 1996. The Australian Soil Classification. CSIRO Publishing, Melbourne, Australia.

Isbell, R.F., 2002. The Australian Soil Classification, rev. ed. CSIRO Publishing, Melbourne, Australia.

Munsell Color, 1988. Munsell Soil Color Charts. Munsell Color, Baltimore, MD.

Sisk, S.J., 1981. NEIC Manual for Groundwater/Subsurface Investigations at Hazardous Waste Sites. EPA-330/9–81–002. U.S. Environmental Protection Agency, Denver, CO.

Testa, S.M., 1994. Geologic Aspects of Hazardous Waste Management. CRC Press, Boca Raton, FL, pp. 145–187.

U.S. Department of Agriculture, Soil Survey Staff, 1999. Soil Taxonomy, 2nd ed. Handbook 436. U.S. Government Printing Office, Washington, DC.

World Reference Base, 2000. WRB for Soil Resources. FAO. http://www.fao.org/ag/ag1/ag11/wrb/doc/wrb2006final.pdf.

11
Acid Drainage Sampling Design and Sample Preparation

BRUCE W. DOWNING

The challenge of sampling is to provide representative and relevant samples, whether the information is being used for acid drainage studies, mineral prospecting, or environmental evaluations. Sampling soil, sediments, or rocks for acid drainage is one of the most important tasks that professional geoscientists and engineers perform in the field.

Introduction

The selection of sample location, number of samples, types of analyses, specific laboratory methods and laboratory reporting limits, and quality assurance and quality control (QA/QC) protocols relates to the objectives of the study and the limitations of the sampling budget. In addition, the samples must be valid as legally defensible scientific evidence if the data are ever discussed in a court of law. For acid rock drainage studies, there are specific objectives for sampling. What constitutes a sample? Here are two definitions: A sample is a "representative fraction of body of material, removed by approved methods, guarded against accidental or fraudulent adulteration, and tested or analyzed in order to determine the nature, composition, percentage of specified constituents, etc. and possibly their reactivity" (American Geological Institute, 1997); and "a small quantity of material relative to the geological mass it represents, collected according to a systematic procedure, of measurable reliability, from which the *acid rock drainage potential* of the mass which it represents may be estimated, based upon appropriate protocols" (Vallee, 1999).

Although in this chapter we focus on acid rock drainage (ARD), an acid drainage evaluation has several goals most of them being identical, whether the assessment is focused on acid mine drainage, ARD associated with pyrite-rich rocks exposed to oxygen and water as part of natural processes or mining or development activities, or acid sulfate soils usually associated with former marine sediments near coastal zones such as southwestern Australia or Viet Nam. The ARD appraisal involves five work stages: deposit definition, project engineering, project economics, production/operation, and reclamation/closure. In each of these stages, there is an element of sampling and analysis to meet environmental requirements. Inherent in sampling is quality assurance and quality control.

Poor sampling techniques and inadequate sample selection can contribute to excessive variance, difficulties in interpretation, and incorrect assessment in an ARD prediction program. As a result of poor sampling there may be serious consequences and costs. Samples must be representative of all geological, lithological, and alteration units related to the mine development plan and be representative of the relative amounts and particle size of each type of material (Steffen, Robertson and Kirsten Inc., 1992); in other words, what are the geological controls on ARD? A sampling program should be designed to be iterative in nature because the presampling notion of what and how much is representative may be shown by the results to be inadequate. Assuming no large-scale changes over time, representative rock or soil samples should be able to provide chemical data that can be reasonably similar to future samples collected in the same vicinity.

The construction of a sound ARD database begins with good sample collection. Appropriate sample

collection, preparation, analytical, and QA/QC procedures must be maintained throughout the project life. Sampling is the single most important aspect of a good survey, for without good sampling, results may not be valid and hence correct interpretations may be difficult to achieve. The essence of sampling is to examine geochemical variation. The proper collection and handling of field samples is the first step toward preventing environmental prosecution and liabilities. This aspect of “legal sampling” is the focus of important training and reference material developed and documented by various organizations (Environment Canada, 2009; MEND, 2010).

The basic components of an ARD sampling program are:

- Design and planning
- Static tests
- Kinetic and humidity cell tests
- Sample types and preparation
- Chemical analysis
- Quality assurance and quality control
- Geological analysis
- Mineralogical analysis
- Pilot-plant tailing analysis
- Data presentation and interpretation
- Complete project oversight by professionally competent personnel

Although sampling costs can be quite expensive, costly remediation and reclamation plans will be based on the results and interpretation of sampling and analysis—hence the importance of a correct assessment. Sampling costs should therefore not predetermine the number of samples taken and analyzed but should depend on the amount necessary to increase confidence in the data and should be considered with regard to exploration, development, and production decisions that rely on sampling results. The number of samples to be taken should be premised on characterization of both waste and nonwaste material. The number of samples will also depend on spatial variation of waste material. Steffen, Robertson and Kirsten (BC), Inc. (1989) developed a curve (Figure 11.1) that can be used as a guideline to ascertain the minimum number of samples required to characterize each geological unit in terms of acid generation and leaching potential. The curve was developed based on a limited number of sites within British Columbia, Canada as a function of the mass of the geological unit being sampled. There are no strict guidelines for establishing sampling protocols; one must judge the best method(s) and be prepared to defend those methods.

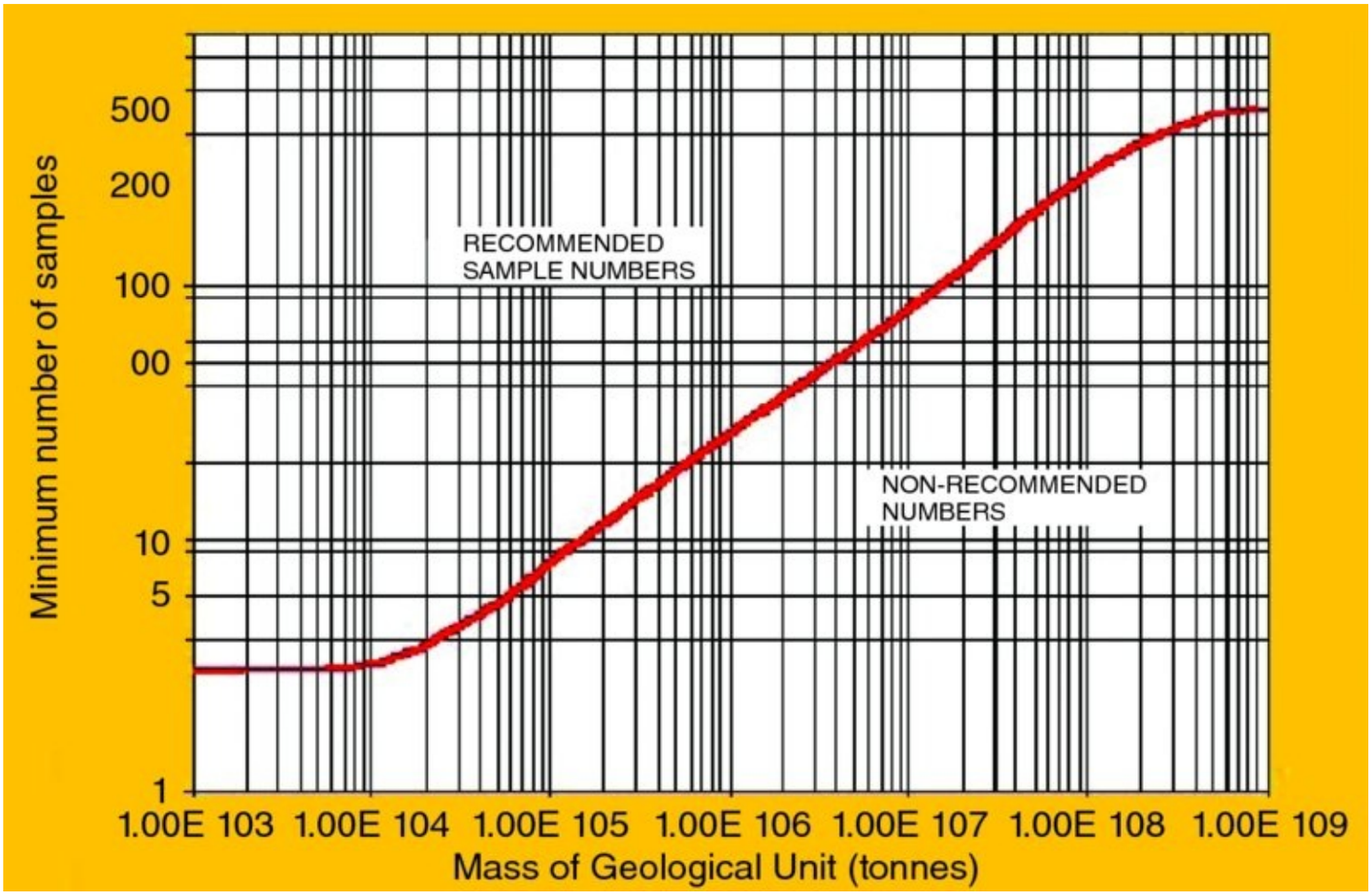


FIGURE 11.1 Hypothetical curve to determine the number of samples required to characterize geological units.

How many samples are enough will also depend on the statistical variation and magnitude of analytical error in the geochemical analysis. Stanley et al. (2010) discuss the geochemical analysis of geological materials and introduction of errors at virtually every stage of sample collection and analysis. Duplicate, replicate, and reference samples must be used in a routine manner to help alleviate some of these errors and provide some confidence in the analysis to monitor and quantify analytical error. Stanley (2010) derived formulas to determine how many samples are necessary to obtain an adequate estimate of the mean of sample measurements. The objective of sampling is to obtain a good estimate of the mean.

Sampling is an integral part of risk assessment and risk management. The initial sampling will help determine if there is a risk, and if so, what variables must be mitigated (i.e., high levels of elements such as arsenic). This initial sampling will also be used as part of the basis for an environmental bond. The ongoing sampling plan will determine the level of mitigation required at closure and if the risk has increased or decreased. Risk assessment and risk management should always be viewed from the initial to the final sampling, which means from baseline survey to closure work.

Design and Planning

The design and planning stage should begin in the early exploration phase. An orientation study is imperative. This study should pay close attention to details in the design that have a bearing on the costs of the major ARD program. Its purpose is to ensure that the proper samples are collected and that proper preparation and chemical analyses are carried out in order to collect as much information as possible and

avoid costly mistakes. The scope of characterization and analysis for each category is shown in Figure 11.2.

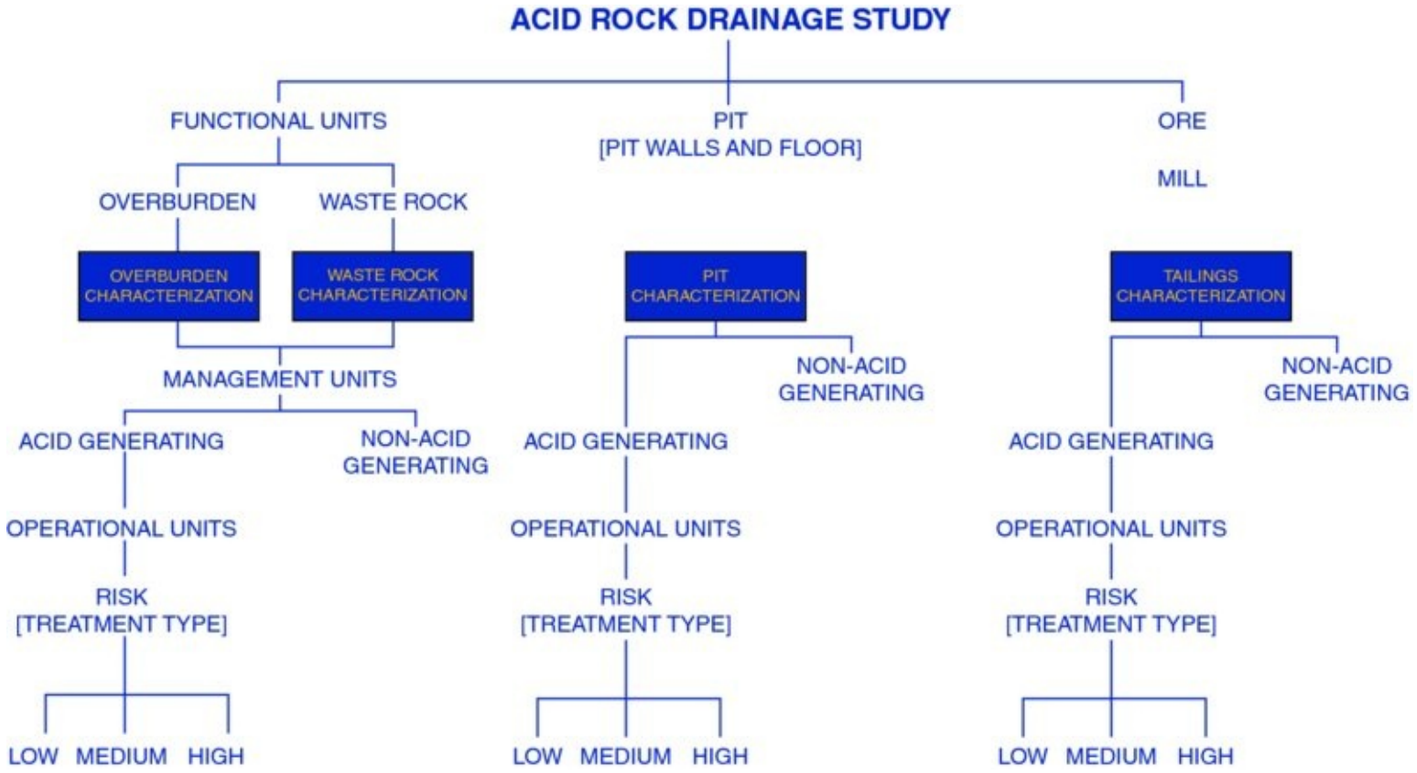


FIGURE 11.2 Scope of characterization and analysis for each mine component.

Continuity is important in the estimation and classification of acid generating and non-acid-generating material. Continuity is essentially composed of two parts: geological continuity and value continuity. *Geological continuity* refers to features that control mineralization; *value continuity* refers to a value or measure such as neutralization potential and the manner in which this variable occurs spatially. Sampling must reflect both these aspects. Sampling detail will depend on whether the program is for a baseline study, Premining plan, Mine operations, or a Reclamation/closure plan.

Sample Types and Sample Preparation

Material sampled can be divided into such categories as overburden (unconsolidated sediments; saprolite in tropical weathering environments), waste rock, and tailings. Rock samples should be obtained from both drill core and outcrop. Samples to be collected should represent all lithologies (Figure 11.3) that are (a) both barren and subore (sulfidic) and (b) altered and nonaltered in order to (1) determine limits of acid–base accounting (ABA) for acid-generating and non-acid-generating material, (2) determine spatial differences in lithologies, and (3) generate enough data points for waste rock block modeling. Waste rock should be defined by a mining engineer. A few ore-grade intervals should also be analyzed as a reference. In general, waste rock composites represent lengths of 10 to 15 m (30 to 45 ft), which conform to minable bench height. Overburden samples should also be composited.

FIGURE 11.3 Note change in color due to alteration; each unit must be sampled.

Sampling programs for a new mine site are likely to be different than those for an existing site. The extent of sampling in an existing site will depend on the information available and the familiarity of site personnel with the geology and distribution of mine rock around the site. The objective of the sampling program will also affect the program. For example, in an existing site, sampling may be done to characterize mine rock types as well as to determine the extent of oxidation, storage of oxidation products, and rock classes within existing waste rock or tailing facilities. The size of each sample depends on the heterogeneity (in particular, the distribution of sulfide and alkali minerals) of the unit being sampled. For static testing a 1-kg sample of a homogeneous unit, at a minimum, is recommended by Steffen, Robertson and Kirsten (BC), Inc. (1989).

Types of Sampling

When deciding on sample spacings and sampling procedures, one must be fully aware of the different levels (or scales) of variability with sampled materials and adjust sample intervals or locations accordingly or use composite samples to represent wide intervals in order to attain a measure of confidence in the intervals between sample locations. Sampling can consist of various types:

- *Point samples:* a single grab sample chosen to represent some mass or random samples taken from various source points, generally within a predetermined area; can be in either two or three dimensions (i.e., dump pile) and composited.
- *Linear samples:* continuous samples over an interval in a line, such as channel samples (Figure 11.4) or drill-hole samples (Figure 11.5) and profile samples of overburden (Figure 11.6).

- *Panel samples:* samples made up of multiple chips collected from a surface with dimensions of 1 to 2 m (3 to 6 ft) (Figure 11.4).
- *Bulk samples:* samples of a large mass of material that will be crushed and split into fractions; may be taken from the various splits.

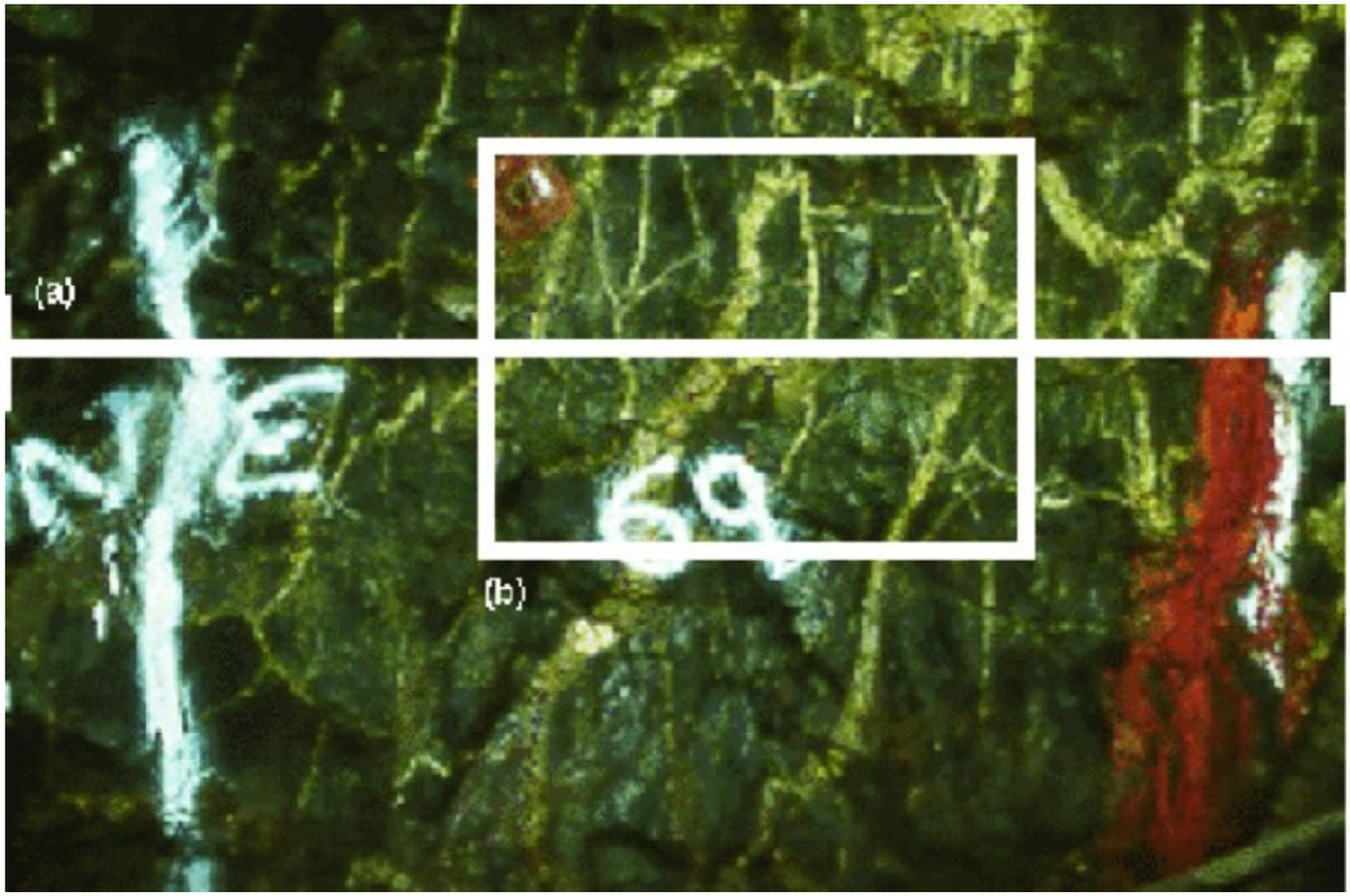


FIGURE 11.4 Linear (a) and panel (b) sample examples.

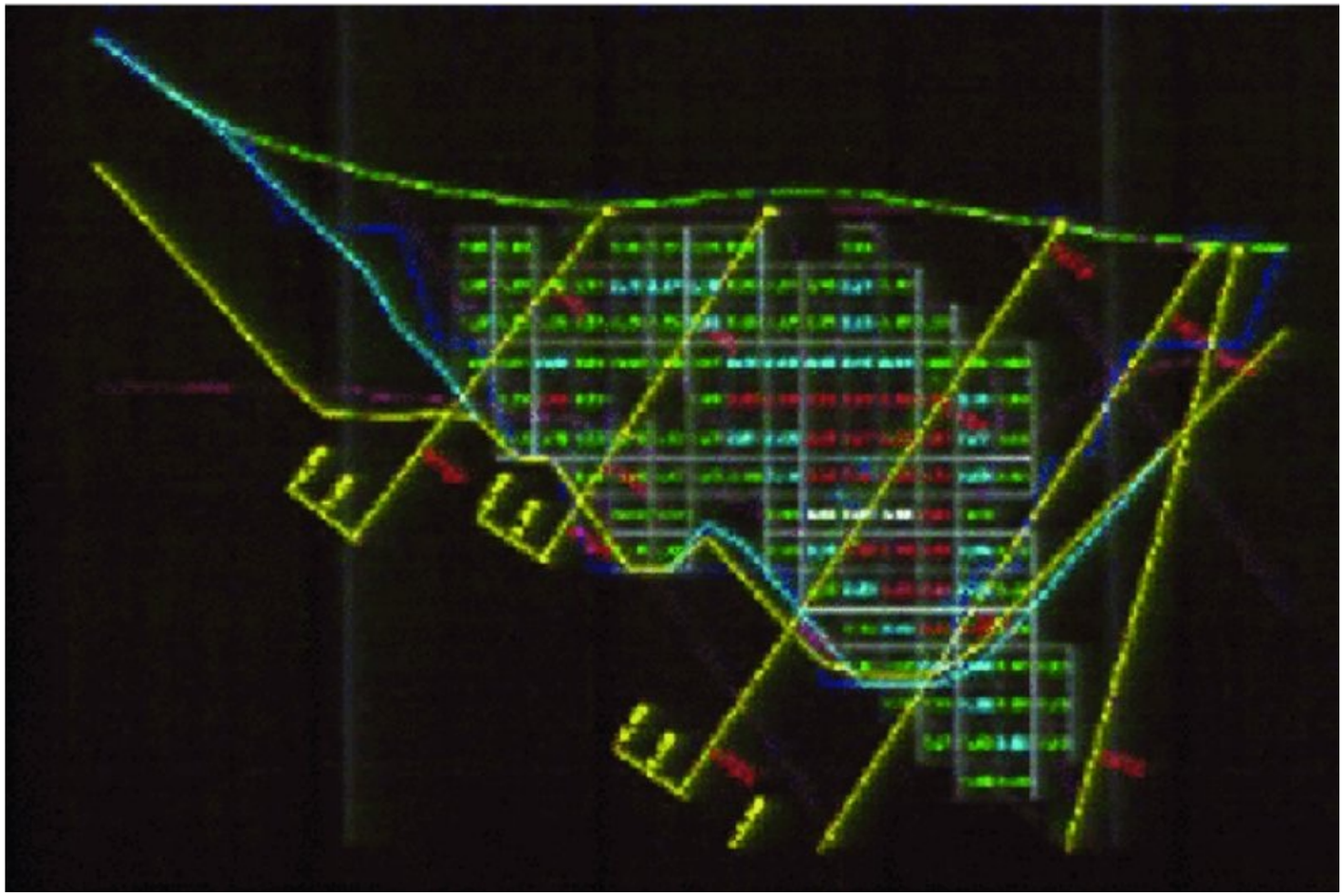


FIGURE 11.5 Drill-hole sampling to generate minable blocks of ore and nonore material. Profile view.

FIGURE 11.6 Profile sample.

Sample Sources

Potential sources for samples for ARD test work at new mines could include:

- Drill cores
- Blast hole cuttings
- Trenches
- Exploration adits
- Bulk sampling for metallurgical testing

In the exploration stage, however, drilling programs typically focus on ore body definition, and therefore additional drilling may be required for detailed characterization of representative waste rock. For existing mines, there are a larger number of sources from which samples could be taken, including:

- Drill core from exploration [can be useful for indication of changes (oxidation) in the period since the rock was extracted]
- Additional drilling
- Pit walls

- Underground workings
- Existing ore stockpiles
- Existing waste rock and tailing facilities

River and Lake Sediment Sampling

In areas affected by mining, it is often advantageous to sample river and lake sediments. These sediments can play an important role in the removal of metals and other contaminants from water. Conversely, they are also a potential source of metal release and toxicity to aquatic organisms that live and feed at the bottom of rivers and lakes (Steffen, Robertson and Kirsten (BC), Inc., 1989). Another source for sampling is soil and stream banks (Figure 11.7). These areas may be more accessible than river and lake sediments and will reflect the geochemistry of underlying lithologies.

FIGURE 11.7 Sample banks (soil and vegetation) on either side to determine possible migration of elements.

This type of sampling is typically not a regular part of an ARD sampling or monitoring program. It may, however, be worthwhile in areas where mine rock is being deposited directly into a water body or where drainage from a mine-affected area carries a contaminant load into receiving waters. Detailed descriptions of sampling methods for this type of material are available. (Environmental Canada, 1983; U.S. Environmental Protection Agency, 1986).

Sampling Equipment

Types of sampling equipment are important when planning and conducting a sampling survey. They range from hand tools such as geological picks, scoops, and shovels to motorized augers and drills. Different

equipment will produce different sample sizes. Be aware of contamination of samples from the use of sampling tools (e.g., by lubricants, paint).

Field Test Work

Field test work of the samples should include paste pH; total dissolved solids, pH, and temperature of water (if present, such as in a stream); photographs of field sites; precise location of the site using a global positioning system (GPS); grid or other survey method; and detailed descriptions of material sampled (Figure 11.8).

FIGURE 11.8 Field test work.

Prior knowledge of overburden (soils) and geological units is very important in determining field sample sites. If such information does not exist, one must be prepared to carry out field mapping. A field measurement often overlooked is bulk specific gravity (density), which is used in estimating the total metal content of a deposit. It is important, specifically in ARD-generating waste material, in determining the number of tons that must be removed and handled. The waste rock will have an economic cutoff grade, so waste material may contain some metals. Generally, each lithological unit will have a different specific gravity, due to variation in mineralogy. There should be enough measurements that a reliable estimate of the error on the mean value can be calculated. Bimodal or skewed distributions of specific gravity measurements indicate the presence of domains or multiple populations and the need to review the various geological categories.

Sample Blending for Waste Piles

In some places there may be a need to create blended waste rock piles and dumps in order to control acid rock drainage. Sampling of material that will be used in a dump is extremely important so as to control the correct blending of waste material. As in the case of systematic grade control, there should also be some systematic waste rock ARD control. Material sampled will most often come from blasthole cuttings. As a result of inappropriate waste rock sampling and subsequent blending practices, the resulting blended pile will be three-dimensionally heterogeneous. The composition of each pile (or sections within the same pile) will be known with poor accuracy and precision, and it may vary from pile to pile.

Sample Handling and Storage

Most samples when collected are put into plastic sample bags or in the case of soil and sediments in kraft paper bags. However, there are times when field samples may need to be submersed and shipped in water or a cold container to prevent any initial rapid oxidation. Such samples may also need to be stored under these conditions until they are not needed. It is generally during sample handling that contamination of the sample may occur.

Samples should be well labeled, with location and type of sample at a minimum. The date and sampler's initials are also recommended. Sample locations should be noted on a site plan and staked or marked in the field where practical. With the advent of GPS units, it is possible to collect coordinates during sampling for recording in a logbook. Photographs of sample locations are also extremely useful.

Chain of Custody

A very important aspect of sampling is the chain of custody from sample collection to shipping and analysis and storage. This chain must be maintained so that any source of contamination and/or errors can be identified and assessed.

Sample Preparation

Sample preparation is the next important step in sampling, whether it is done in the field or in the laboratory. It is during sample preparation that some contamination of the sample may occur. All field and laboratory sample preparation procedures must be documented in detail in the ARD report.

Sample Composite Procedures

- *Pulps*. Pulps that are used for assaying can also be used for ABA, assuming that the waste sections were assayed in conjunction with mineralized sections. By using these assay pulps, considerable time and expense can be saved. Pulps for the intervals specified are requested from the analytical laboratory by sample number. An equal weighed amount of each pulp is taken from each sample envelope and then combined, forming a composite sample over a specified interval. From this composite, the subsamples are taken for various analyses.
- *Rejects*. Reject samples from assay sample preparation can also be used for ABA analyses and kinetic and humidity cell test work. Compositing rejects must be done as described in the procedure discribed above.
- *Sampling theory*. Pierre Gy developed a sampling theory that essentially addresses the fundamental questions of sampling broken material. François-Bongarcon has revisited Gy's theory with some further refinements. Sketchley has taken Gy's formula and developed the sample constant into a sampling nomograph (see Gy, 1982, 1992, 1998; François-Bongarcon, 1999; Sketchley, 1999).

- *Common sampling problems*. Types of problems that lead to the collection of unsatisfactory data generally arise from the sampling program, such as:
  - Inappropriate sample type.
  - Insufficient samples taken to properly characterize the waste material with regard to sample variability.
  - Inappropriate field sample spacing and size for waste material characterization; representative subsamples are not obtained, due to laboratory sampling procedures that reduce field sample mass at too coarse a particle size.
  - Representative subsample analyses not obtained because the analytical sample size is too small.

Sources of Error

The ARD practitioner must recognize that there will be sources of error (measurement errors) resulting from both sampling and analysis. Errors are not “mistakes” but refer to inevitable inaccuracies and imprecision of data resulting from limitations of selecting small representative samples from large volumes of material and from the sensitivity of analytical methods. As errors are cumulative, each step of sampling through to analysis can be identified as a source of error. QA/QC programs will help to minimize these errors but will not eliminate them. The treatment of errors is discussed by Stanley and Bloom, and the reader is referred to their papers (Bloom, 1999; Stanley, 1999). In any ARD report, these errors must be identified and presented to the reader. Statistical treatment of the data with respect to sampling should also be discussed.

Chemical Analysis

Before analyses are carried out, the ARD practitioner must discuss with the analytical laboratory the appropriate chemical analyses and methods of sample preparation and digestion. The amount of sample used in the analysis is very important, as variation in sample mass may cause analytical variation.

Geological Analysis

Geological sampling will include both regional and detailed mapping and sampling. This should also incorporate overburden and soil mapping and sampling, as these materials may be used for construction purposes and/or reclamation.

Mineralogical Analysis

Neutralization potential values alone can never represent the compositional, structural, and textural nature of waste material. A detailed mineralogical study will provide insight into grain-size distributions, mineral assemblages, spatial variations in assemblages, and so on. Mineralogical mapping and sampling must be carried out in conjunction with the geological analysis.

Pilot and Milling Plant Sampling

The milling plant is the best place to obtain a representative sample of both broken rock and tails. The broken rock material is usually crushed to 35 to 20 mm before entering the grinding circuit. Tailings will be produced after the beneficiation stage. Samples should be taken on a regular basis so as to obtain information on material going to the heap leach pads or to the tailings impoundment. In the pilot plant, testing the material will achieve two purposes: (1) ARD characterization of potential leaching material

and tailings, and (2) determination of sampling procedures for the milling plant.

Data Presentation, Interpretation, and Reporting

The various analytical methods applied to samples will produce numerous data. Extreme care should be taken in the application of statistical analysis. Poor understanding of the statistical aspects of data evaluation will lead to incorrect (potentially expensive) conclusions. The question that needs to be addressed by the ARD practitioner is: How defensible are my data? The ARD report must include all aspects of sampling so that the regulator and other interested parties have confidence in the results, interpretations, and conclusions.

Qualified Personnel and the Sampling Program

Sample programs must be conducted by qualified professionals, who must have some geochemical training. This aspect is very important, as all too often, unqualified personnel take samples without input from a geochemist.

Conclusions

Well-planned-out sampling is the basis of defensible data, good interpretation, and viable conclusions. Qualified professionals should be involved in the design, planning, and supervision of a sampling program that will give regulators, stakeholders, and the public confidence in the results.

References and Suggested Reading

American Geological Institute, 1997. Dictionary of Mining, Mineral and Related Terms, 2nd ed. U.S. Bureau of Mines Special Publication. U.S. Department of the Interior, Washington, DC, 646 pp.

Bloom, L., 1999. Third party vetting of geochemical programs or return on quality. In: Short Course on Quality Control in Mineral Exploration. Presented at the 19th International Geochemical Exploration Symposium, April 11, Vancouver, BC, Canada.

Environment Canada, Water Quality Branch, 1983. Sampling for Water Quality. Inland Waters Directorate, Ottawa, ON, Canada.

Environment Canada, 2009. Guidance for the Reporting of Tailings and Waste Rock to the National Pollutant Release Inventory (Version 1.4). http://www.ec.gc.ca/inrp-npri/default.asp?lang=En&n=C115DEB3-1, 31 pp.

François-Bongarcon, D., 1999. Extensions to the demonstration of Gy's formula. Exploration and Mining Geology, vol. 7, no. 1–2, pp. 149–155.

Gy, P. 1982. Sampling of Particulate Materials: Theory and Practice. Elsevier, Amsterdam, 431 pp.

Gy, P., 1992. The Sampling of Heterogeneous and Dynamic Material Systems. Elsevier, Amsterdam, 653 pp.

Gy, P., 1998. Sampling for Analytical Purposes. Wiley, New York, 150 pp.

MEND (Mine Environment Neutral Drainage), 2010. http://www.nrcan.gc.ca/mms-smm/tect-tech/sat-set/med-ndd-eng.htm; the website features guidelines and manuals.

Sketchley, D.A., 1999. Gold deposits: establishing sampling protocols and monitoring quality control. Exploration and Mining Geology, vol. 7, no. 1–2, pp. 129–139.

Stanley, C., 1999. Treatment of geochemical data: some pitfalls in graphical analysis. In: Short Course on Quality Control in Mineral Exploration. Presented at the 19th International Geochemical Exploration Symposium, April 11, Vancouver, BC, Canada.

Stanley, C., 2010. How many samples are enough? Explore, no. 148, pp. 2–10.

Stanley, C., O'Driscoll, N., and Ranjan, P., 2010. Determining the magnitude of true analytical error in geochemical analysis. Geochemistry Exploration, Environment, Analysis, vol. 10, pp. 355–364.

Steffen, Robertson and Kirsten (BC), Inc., 1989. Study in association with Norecol Environmental Consultants and Gormely Process Engineering. Draft Acid Rock Drainage Technical Guide. Prepared for British Columbia Acid Mine Drainage Task Force, vols. I and II.

Steffen, Robertson and Kirsten (BC), Inc., 1992. Mine Rock Guidelines: Design and Control of Drainage Water Quality. Report prepared for the Saskatchewan Environment and Public Safety, Mines Pollution Control Branch.

U.S. Environmental Protection Agency, 1986. Handbook: Stream Sampling for Waste Load Allocation Applications. EPA/625/6-86/013. U.S. EPA, Washington, DC.

Vallee, M., 1999. Sampling quality control. Exploration and Mining Geology, vol. 7, no. 1–2.

12
Acid Drainage and Aquatic Resources

DENNIS R. NEUMAN, STUART R. JENNINGS, AND JAMES A. JACOBS

Evaluating acid mine drainage and the effects on fish health and ecology is an important aspect of environmental science and aquatic resources management. Resulting low-pH conditions from acid mine drainage mobilize metals from mining waste materials and pyrite-rich rocks and soils, usually resulting in degradation of water quality and impairment of aquatic health. Acid mine drainage and associated weathering products commonly result in physical, chemical, and biological impairment of surface water. Evidence from literature and field observations of practices to date suggests that large-scale mining or land development in sulfide-hosted rock imparts a substantial and unquantifiable environmental risk to surface water quality and fisheries (Jennings et al., 2008). Opportunities exist for significantly improved acid drainage prevention methods, remediation technologies, and environmental practices.

Introduction

Acidic drainage occurs when sulfide-bearing materials are exposed to water and oxygen, allowing mineral weathering reactions to proceed, including oxidation and hydrolysis. Mining increases the exposed surface area of sulfur-bearing rocks, allowing for accelerated sulfuric acid generation. If insufficient buffering capacity is present as neutralizing minerals such as calcite ($CaCO_3$), soil and water resources may become acidified. Collectively, the generation of sulfuric acid from pyrite and other sulfide minerals is termed *acid drainage* (AD).

Although other acid drainage conditions do exist in nature and as acid sulfate soils, or through other anthropogenic activities, such as development or farming, the majority of acid drainage is caused by mining activities. Having much greater surface area than in-place geologic material due to their smaller grain size, mine tailings and waste rock are more prone to generating acid drainage. Since large masses of sulfide minerals are exposed quickly during the mining and milling processes, the surrounding environment can sometimes not attenuate the resulting low-pH conditions. Metals that were once part of the host rock are solubilized and exacerbate the deleterious effect of low pH on terrestrial and aquatic receptors. Concentrations of common elements such as Cu, Zn, Al, Fe, and Mn all increase dramatically in waters with low pH. Logarithmic increases in metal levels in waters from sulfide-rich mining environments are common where surface water or groundwater pH is depressed by acid generation from sulfide minerals. These environmental, human health, and fiscal consequences, if not mitigated, can have long-lasting effects (U.S. EPA, 1995).

Acid mine drainage continues to emanate from mines in Europe established during the Roman Empire prior to A.D. 467 (Center for Streamside Studies, 2002). Georgius Agricola's *De Re Metallica* (1556), the first and seminal treatise on mining, exhibits detailed woodcut illustrations not only of the known mechanics of sixteenth-century mining, but also depictions of the devastation of streams. The cost of mitigation of environmental damage from acid mine drainage is great. In 1993, the U.S. Forest Service estimated that between 20,000 and 50,000 mines are currently generating acid on lands managed by that agency, with negative impacts from these mines affecting some 8000 to 16,000 km of streams (U.S. Department of Agriculture, 1993). Since that estimate, the numbers of mines generating acid mine

drainage and the associated negative impacts on streams have grown significantly. Many of these mines are small abandoned facilities located in remote areas of the western United States and originating prior to modern environmental controls. However, several large-scale mines developed in the latter half of the twentieth century have declared bankruptcy and left taxpayers with the responsibility of treating acid waters in perpetuity. Examples include the Zortman Landusky mine in Montana, the Summitville mine in Colorado, and the Brohm mine in South Dakota. The largest and most expensive sites that the U.S. Environmental Protection Agency (EPA) has listed under the Comprehensive Environmental Resource Compensation and Liability ACT (CERCLA; a.k.a. the Superfund) are mining sites in the West, including the Iron Mountain mine in California, Bunker Hill in Idaho, and the Butte--Clark Fork River complex in southwestern Montana. Human health risks and ecological injury, chiefly from elevated metals, have been identified by the EPA and natural resource trustees at many of these mining Superfund megasites.

Acidic drainage has been identified as the largest environmental liability facing the Canadian mining industry and is estimated at $2 billion to $5 billion (MEND, 2001). In response to the challenge presented by mitigation of AD, 200 technology-based reports were generated to evaluate sampling, prediction, prevention, treatment, and monitoring of potentially acid-generating materials and locations. A 1986 estimate for Canada suggests that acid-generating tailings cover 12,000 ha, and an additional 350 million tons of mine waste rock was noted (Price, 2001).

Effect of Acid Mine Drainage on Aquatic Resources

Once acid drainage is created, metals are released into the surrounding environment and become readily available to biological organisms. In water, for example, when fish are exposed directly to metals and H^+ ions through their gills, impaired respiration may result from chronic and acute toxicity. Fish are also exposed indirectly to metals through ingestion of contaminated sediments and food items. A common weathering product of sulfide oxidation is the formation of iron hydroxide [$Fe(OH)_3$], a red-orange precipitate found in thousands of miles of streams affected by acid drainage. Iron hydroxides and oxyhydroxides may physically coat the surface of stream sediments and streambeds destroying habitat, diminishing the availability of clean gravels used for spawning and reducing fish food items such as benthic macroinvertebrates. Acid mine drainage, characterized by acidic metalliferous conditions in water, is responsible for physical, chemical, and biological degradation of stream habitat. Two reports describe acid mine drainage on aquatic resources (Jennings et al., 2008; Neuman et al., 2009).

Water contaminated by acid drainage, often containing elevated concentrations of metals, can be toxic to aquatic organisms, leaving receiving streams devoid of most living creatures (Kimmel, 1983). Receiving waters may have a pH value as low as 2.0 to 4.5, levels toxic to most forms of aquatic life (Hill, 1974). Data relating to specific effects of low pH on growth and reproduction (Fromm, 1980) may be related to calcium metabolism and protein synthesis. Fromm (1980) suggested that a “no effects” level of pH for successful reproduction is near 6.5, while most fish species are not affected when the pH is in the range 5.5 to 10.5. Howells et al. (1983) reported that interactions of pH, calcium, and aluminum may be important to understanding the overall effects on fish survival and productivity. Several reports indicate that low-pH conditions alter gill membranes or change gill mucus, resulting in death due to hypoxia. Hatchery-raised salmonids can tolerate pH 5.0, but below this level, homeostatic electrolyte and osmotic mechanisms become impaired (Fromm, 1980).

A study of the distribution of fish in Pennsylvania streams affected by acid mine drainage (Cooper and Wagner, 1973) found fish to be affected severely at pH 4.5 to 5.5. Ten species revealed some tolerance to acid conditions of pH 5.5 and below; 38 species were found living in waters with pH values ranging from

5.6 to 6.4; and 68 species were found only at pH levels greater than 6.4. Further, these investigators reported complete loss of fish in 90% of streams with waters of pH 4.5 and a total acidity of 15 mg/L.

Healthy, unpolluted streams generally support several species and a moderate abundance of individuals, whereas streams affected are dominated by fewer species and often low-to-moderate numbers of organisms. Streams affected by acid mine drainage are poor in taxa richness and abundance. In older studies (Warner, 1971), more species of insects and algae were found in unpolluted West Virginia streams (pH > 4.5) than in streams polluted by acid (pH 2.8 to 3.8). Reductions of benthic fauna in a West Virginia stream severely affected by acid mine water were reported by Menendez (1978). In more recent studies (Farag et al., 2003), some streams in the Boulder River watershed in Montana affected by nearly 300 abandoned metal mines are devoid of all fish near mine sources. Populations of brook trout *(Salvelinus fontinalis)*, rainbow trout (*Oncorhynchus mykiss)*, and cutthroat trout (*Oncorhynchus clarki)* were found farther downstream and away from sources of acid mine drainage. In a 2003 study evaluating the effect on the population structure of salmon of localized habitat degradation from a gold mine near the Yukon River in central Alaska, it was suggested that coho salmon (*Oncorhynchus kisutch)* may be at risk of losing genetic diversity due to localized habitat degradation (Olsen et al., 2004a,b). The abandoned Britannia copper mine in British Columbia, Canada has been releasing acid mine drainage into local waters for many years. Investigators compared fish abundance, distribution, and survival at contaminated and noncontaminated areas (Barry et al., 2000). Chum salmon (*Oncorhynchus keta)* fry abundance was significantly lower near the waters affected (pH < 6 and dissolved copper > 1 mg/L) than in the reference area. The investigators also reported that laboratory bioassays confirmed that acid mine drainage from the Britannia mine was toxic to juvenile chinook salmon (*Oncorhynchus tshawytscha)* and chum salmon. Chinook salmon smolt transplanted to surface cages near Britannia Creek experienced 100% mortality within 2 days (Barry et al., 2000).

The scientific literature is replete with studies designed to quantify the adverse environmental effects of acid mine drainage on aquatic resources. Most recent investigations focus on multiple bioassessments of large watersheds. These assessments include water and sediment chemistry, benthic macroinvertebrate sampling for taxa richness and abundance, laboratory acute water column evaluations, laboratory chronic sediment testing, caged fish within affected streams, and development of models to explain and predict the impact of acid mine drainage on various aquatic species Johnson et al., 1987; Woodward et al., 1997; Beltman et al., 1999; Hansen et al., 1999, 2002; Baldigo and Lawrence, 2000; Soucek et al., 2000; Kaeser and Sharpe, 2001; Maret and MacCoy, 2002; Schmidt et al., 2002; Griffith et al., 2004; Boudou et al., 2005; Martin and Goldblatt, 2007.

The ecological effects of acidic waters that are generated due to the oxidation of pyrite and related sulfide minerals, regardless of the source, are most clearly seen in aquatic environments such as streams, lakes, and marshes. In addition to the input from acid drainage, acid rain from atmospheric pollution is another source of acidity. Acid rain is formed from oxidized sulfur particles caused by the burning of coal and petroleum hydrocarbons containing high levels of sulfur. Most lakes and streams have a natural or background pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid drainage or acid rain. Although acid rain is a regional atmospheric environmental challenge and has caused documented fish kills and wildlife species endangerment, acid drainage tends to be much more localized and causing more impairment to specific aquatic species in the closest streams, rivers, lakes, and wetlands adjacent to sources of acid generation.

Fish and Aquatic Organisms in Acid Waters

Regardless of the source, sulfuric acid causes a cascade of effects that harm or kill individual fish, reduce

or eliminate fish populations, and decrease biodiversity in the areas affected. As sulfuric acid from acid drainage (or acid rain) flows through soils in a watershed, aluminum and possibly other heavy metals are released from the soils into the streams, lakes, and rivers located in that watershed.

As pH in a water body decreases with the input of sulfuric acid, metals in sediments tend to solubilize and enter the water column. With increasing acidity levels, aluminum and other metal levels tend to increase, as does the toxicity of the aquatic environment to a large variety of organisms. Both low pH and increased aluminum levels are directly toxic to many fish species and other organisms. A gradual lowering of pH and gradual increase in aluminum levels cause chronic stress that may not kill individual fish, but leads to generally lower body weight and smaller size. These responses to gradual or seasonal environmental changes make affected fish less able to compete for food and habitat, causing declines in species diversity as well as abundance.

Some species or populations of plants and animals are able to tolerate acidic waters from acid drainage. Metal tolerance is known in both plants and animals. Others, however, are acid-sensitive. Generally, the young of most species are more sensitive than adults to environmental conditions. Rapid changes in pH and metal concentrations have a more pronounced negative result than does gradational or seasonal change. At pH 5, most fish eggs cannot hatch. At lower pH levels, some adult fish die. Some acid lakes have no fish. Figure 12.1 shows that not all fish, shellfish, or the insects that they eat can tolerate the same amount of acid; for example, frogs can tolerate water that is more acidic (i.e., has a lower pH) than can trout.

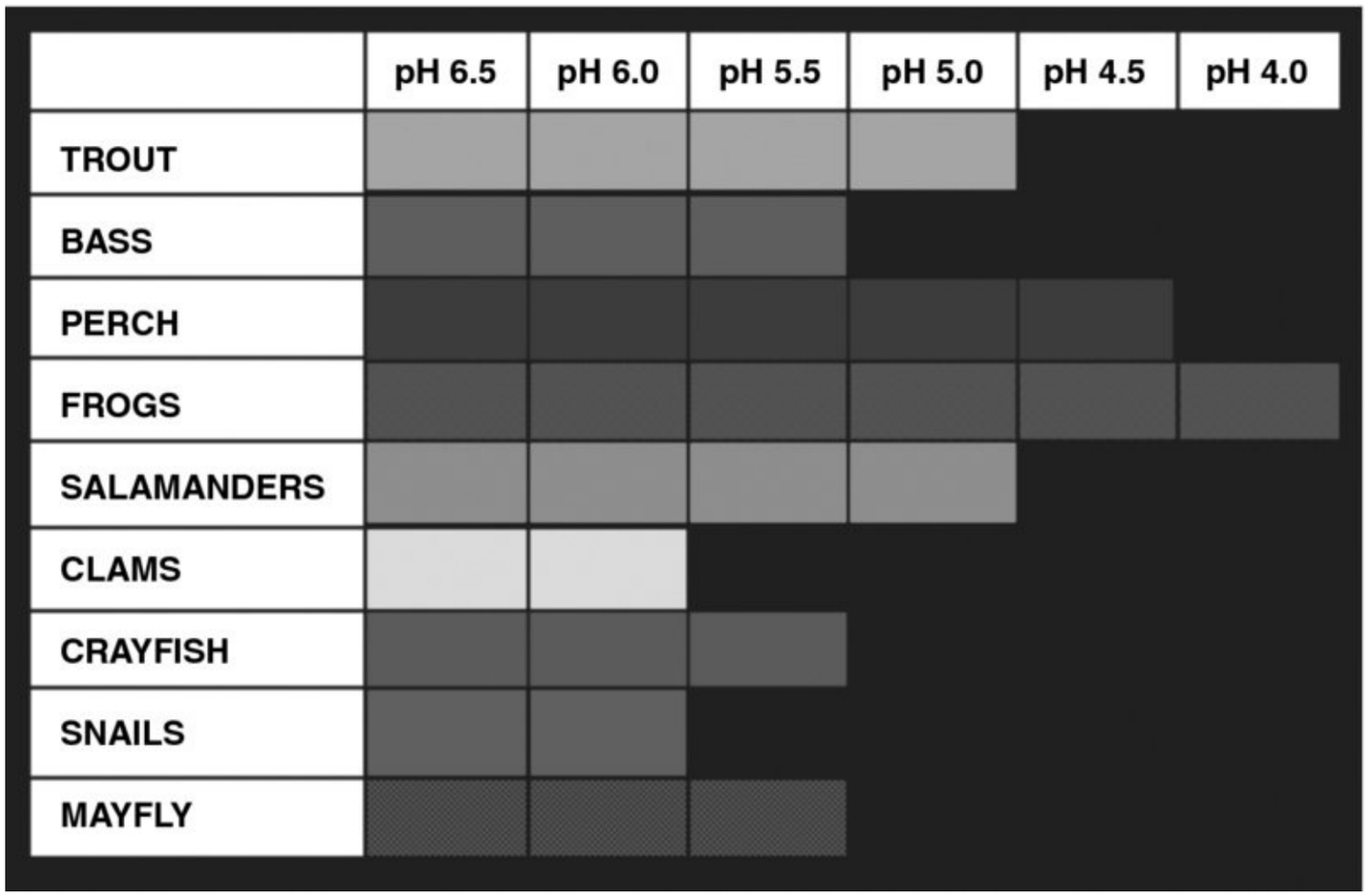


FIGURE 12.1 Estimated survival of various organisms related to pH. (From U.S. Environmental Protection Agency, 2010.)

Ecosystem Changes to Acid Waters

An ecosystem is a *biological environment* consisting of all the *organisms* living in a particular area, as well as all the nonliving, physical components of the environment with which the organisms interact, such as air, soil, water, and sunlight. The plants and animals living within an ecosystem are highly interdependent. For example, frogs may tolerate relatively high levels of acidity, but if their diet is made up of organisms intolerant of acidity, they may be affected because part of their food supply may disappear. Because of the connections between the many fish, plants, and other organisms living in an aquatic ecosystem, changes in pH or aluminum levels affect biodiversity as well. Thus, as lakes and streams become more acidic, the numbers and types of fish and other aquatic plants and animals that live in these waters decrease.

Acid Drainage and Fish Kills

There are thousands of site increases in acidity, and metal concentrations in surface water have killed fish on a large scale as a direct result of acid mine drainage. Following are three case examples.

Case Study 1: Leviathan Mine, Alpine County, California

Prior to mining development in the 1870s, the Leviathan mine area was once known for Sierra trout fishing in the local mountain streams and creeks. Although the destruction of a once vibrant fish population in Leviathan Creek is just one casualty of acid drainage development, the case history of the Leviathan mine is common among inactive metals mines in the western United States. According to the U.S. Environmental Protection Agency (2000), the Leviathan mine site is an abandoned sulfur mine located on the eastern slope of the Sierra Nevada in Alpine County, California at about 7000 ft above sea level. The mine began operations in 1863 for the extraction of copper sulfate for processing silver ore in the Comstock mining region of Nevada. Mining operations ceased in 1872, due to the high sulfur and low copper content of the ore. It is the high sulfur content that has since contributed to the massive acid mine drainage issue.

With larger equipment and different economics, in 1954 the Anaconda Company transformed the underground workings into an open-pit mine to extract the sulfur ore. Approximately 22 million tons of overburden and waste rock was removed to get to the sulfur ore. Anaconda placed the sulfur ore into and along the channels of Leviathan and Aspen creeks. In 1962 the Anaconda Company sold the mine to Alpine Mining Enterprises. The mine has not been active since 1962.

Infiltration of rainwater into and through the open pit and overburden piles created acid mine drainage that discharges directly into Leviathan Creek. Water contact with the mining waste piles located in the creek itself has also contaminated Leviathan Creek. The low-pH and high metals content of the acid mine drainage have eliminated aquatic life in Leviathan and Bryant creeks downstream of the mine. The release of acid mine drainage from the site has resulted in fish kills in Leviathan and Bryant creeks and the East Fork of the Carson River, which is 10 miles downstream of the site. The creeks and river downstream from the mine are historical habitat for the Lahontan cutthroat trout (*Onchorhynchus clarki henshawi*), a federally listed endangered species. Cutthroat trout still inhabit the East Fork of the Carson River (U.S. Environmental Protection Agency, 2000). Full remediation of Leviathan Creek and the inactive mine site are unfunded and decades away.

Health risks to wildlife in this case are not well documented. Risk assessments by the California Department of Health Services found that past and present consumption of water from the Leviathan, Aspen, and Bryant creeks and the River Ranch irrigation channel downstream of the Leviathan mine

posed both cancer and noncancer health risks to humans from exposure to arsenic. Swimming and wading in these creeks pose human health risks due to arsenic exposure, which was mobilized by low-pH waters. A general lack of toxicological data exists and there are significant uncertainties regarding human consumption of fish, plants, and wild game collected near the Leviathan mine, or eating beef raised nearby. Inhalation of dust near the mine, and future exposure to surface water and sediments by drinking, swimming, and wading in affected water bodies are persistent concerns.

Case Study 2: Iron Mountain, Shasta County, California

Chinook salmon runs have been documented historically and currently in surface waters near Mount Shasta, about 62 miles north of Redding, California. The Richmond mine at Iron Mountain is about 9 miles northwest of Redding. In more recent times, the Iron Mountain mine has shown the full extent of acid mine drainage characteristics and significant environmental degradation. In 1983, the Richmond mine at Iron Mountain was added to the U.S. Environmental Protection Agency (EPA) Superfund site list. Based on U.S. EPA documents (2010), from the 1860s through 1963, the 4400-acre Iron Mountain mine site was mined periodically for iron, silver, gold, copper, zinc, and pyrite. Although mining operations were discontinued in 1963, underground mine workings, waste rock dumps, piles of mine tailings, and an open mine pit remain at the site. Historic mining activity at the Iron Mountain mine has fractured the mountain, exposing pyrite to surface water, rainwater, and oxygen and leading to the formation of sulfuric acid. Biogeochemical research by Edwards et al. (2000) describes in detail the biological aspects of sulfide mineral dissolution that contribute to acid mine drainage at the Iron Mountain mine. Sulfuric acid flows through Iron Mountain and leaches out a variety of metals, including copper, cadmium, zinc, and other metals. High-concentration sulfuric acid flows out of seeps and portals at the mine.

Nordstrom et al. (2000) documented a pH of −3.6 in waters from the Richmond mine. Much of the acidic mine drainage is ultimately channeled into Spring Creek Reservoir by creeks surrounding the Iron Mountain mine. The Bureau of Reclamation releases the stored acid mine drainage periodically into Keswick Reservoir. Planned releases are timed to coincide with the presence of diluting releases of water from Shasta Dam. On occasion, uncontrolled spills and excessive waste releases have occurred when Spring Creek Reservoir reached capacity. Without sufficient dilution, harmful quantities of metals are introduced into the Sacramento River. Approximately 70,000 people use surface water within 3 miles of the Iron Mountain mine as their primary source of drinking water. The low pH level and companion metal contamination from the mine have caused the virtual elimination of aquatic life, including fish, in sections of Slickrock, Boulder, and Spring creeks. Since 1940, high levels of contamination in the Sacramento River have caused numerous documented fish kills. The continuous release of metals from the Iron Mountain mine has contributed to a steady decline in the fisheries population in the Sacramento River. In 1989, the National Marine Fisheries Service took emergency action to list the winter run chinook salmon as threatened under the Endangered Species Act and to designate the Sacramento River from the Red Bluff diversion dam to the Keswick dam as a critical habitat. In January 1994, the National Marine Fisheries Services issued its final rule, reclassifying the winter run chinook salmon as an endangered species.

Case Study 3: Blue Creek, Kanawha County, West Virginia

According to the local newspaper (McCoy, 2010) a spill of iron-laden acidic mine drainage has caused a fish kill along 9 miles of Blue Creek, a high-quality bass and trout stream in eastern Kanawha County in West Virginia. The spill began on October 2 or 3, 2010 in a small headwater tributary known as Morris Fork. Dead fish were documented in Blue Creek downstream of the town of Coco, West Virginia. A district fisheries biologist for the state Division of Natural Resources noted that it was a state-government

attempt to clean up an abandoned coal mine that actually caused the spill. The hazmat workers tried to remediate an inactive mine water storage basin. According to reports, an underestimate of the total volume of the impounded water was the cause of the spill. Although the spilled water was not acidic when the release occurred, the water became more acidic over time as more water flowed out of the impoundment. It took a week before the leaking water started producing sulfuric acid and soluble iron to the extent that dead fish were observed and documented. An inventory of the dead fish was performed, and 13- to 15-in. smallmouth bass were among the dead fish. Other lost fish included rock bass as well as other assorted species. Blue Creek is reportedly stocked with brown trout fingerlings. Although dead trout were not found during the initial dead fish inventory, the trout were probably killed higher up in the watershed than in the area inspected by fish biologists. The acid drainage spill was stopped 9 miles downstream from the impoundment by placing limestone sand into the stream. The limestone buffered the sulfuric acid and prevented more fish from being killed.

Nitrogen and Acid Waters

Fish kills associated with acidic water can also occur when a body of water becomes eutrophic (oxygen depleted). Although the role of nitrogen in acid rain is well documented, the potential for nitrogen compounds to interact with acid drainage is also possible in areas where sulfuric acid is generated from pyrite oxidation and mixes with storm water runoff from nearby agricultural lands that may contain excessive fertilizers and nitrates. According to the U.S. EPA, storm runoff rich in nitrates represents 55 to 90% of the nitrogen produced by various human activities. This nitrate-rich runoff reaches estuaries and coastal ecosystems and is transported and deposited via surface waters and groundwater. Nitrogen introduced to water bodies as nitrates is an important factor in causing eutrophication of lakes and rivers. The symptoms of eutrophication include blooms of algae (both toxic and nontoxic), decline in the health of fish and shellfish, loss of seagrass beds and coral reefs, and ecological changes in food webs. Under certain unfortunate circumstances, nitrate-rich waters from agricultural tracts can mix with waters containing acid drainage to decrease the pH of the water and increase the potential for fish kills and significant environmental degradation.

Problems and Questions

1. Describe the mechanism by which acid drainage develops and moves into an aquatic environment.
2. Based on Figure 12.1 is it likely that salamanders will survive at pH 4? Explain why.
3. Together, what are biological organisms and the environment called?
4. What causes death by eutrophication?
5. A gradual lowering of pH and gradual increase in aluminum levels in surface waters cause chronic stress that may not kill individual fish but lead to what physiological challenge for the fish?
6. Healthy, unpolluted streams generally support several species of fish or other organisms and moderate abundance of individuals. What dominates streams affected by acid drainage?

References and Suggested Reading

Agricola, G., 1556. De Re Metallica. Translated in 1912 by H.C. Hoover and L.H. Hoover. Republished by Dover, New York, 1950, 572 pp.

Baldigo, B.P., and Lawrence, G.B., 2000. Composition of fish communities in relation to stream acidification and habitat in the Neversink River, New York. Transactions of the American Fisheries Society, vol. 129, no. 1, pp. 60–76.

Barry, K.L., Grout, J.A., Levings, C.D., Nidle, B.H., and Piercey, G.E., 2000. Impacts of acid mine drainage on juvenile salmonids in an estuary near Britannia Beach in Howe Sound, British Columbia. Canadian Journal of Fisheries and Aquatic Sciences vol. 57, no. 10, pp. 2031–2043.

Beltman, D.J., Clements, W.H., Lipton, J., and Cacela, D., 1999. Benthic invertebrate metals exposure, accumulation, and community level effects downstream from a hard rock mine site. Environmental Toxicology and Chemistry vol. 18, no. 2, pp. 299–307.

Boudou, A., Maury-Brachet, R., Coquery, M., Durrieu, G., and Cossa, D., 2005. Synergic effect of gold mining and damming on mercury contamination in fish. Environmental Science and Technology, vol. 39, no. 8, pp. 2448–2454.

Center for Streamside Studies, 2002. Environmental Impacts of Hardrock Mining in Eastern Washington. College of Forest Resources and Ocean and Fishery Sciences, University of Washington, Seattle, WA.

Cooper, E.L., and Wagner, C.C., 1973. The effects of acid mine drainage on fish populations. In: Fish and Food Organisms in Acid Waters of Pennsylvania. EPA-R#-73–032. U.S. Environmental Protection Agency, Washington, DC, 114 pp.

Edwards, K.J., Bond, P.L., Druschell, G.K., McGuire, M.M., Hamers, R.J., and Banfield, J.F., 2000. Geochemical and biological aspects of sulfide mineral dissolution: lessons from Iron Mountain, California. Chemical Geology, vol. 169, no. 3–4, pp. 383–397.

Farag, A.M., Skaar, D., Nimick, D.A., MacConnell, E., and Hogstrand, C., 2003. Characterizing aquatic health using salmonids mortality, physiology, and biomass estimates in streams with elevated concentrations of arsenic, cadmium, copper, lead, and zinc in the Boulder River watershed, Montana. Transactions of the American Fisheries Society, vol. 132, no. 3, pp. 450–457.

Fromm, P.O., 1980. A review of some physiological and toxicological responses of freshwater fish to acid stress. Environmental Biology of Fishes, vol. 5 no. 1, pp. 79–93.

Griffith, M.B., Lazorchak, J.M., and Herlihy, A.T., 2004. Relationships among exceedances of metals criteria, the results of ambient bioassays, and community metrics in mining impacted streams. Environmental Toxicology and Chemistry, vol. 23, no. 7, pp. 1786–1795.

Hansen, J.A., Woodward, D.F., Little, E.E., DeLonay, A.J., and Bergman, H.L., 1999. Behavioral avoidance: possible mechanism for explaining abundance and distribution of trout in a metals-impacted river. Environmental Toxicology and Chemistry, vol. 18, no. 2, pp. 313--317.

Hansen, J.A., Welsh, P.G., Lipton, J., and Cacela, D., 2002. Effects of copper exposure on growth and survival of juvenile bull trout. Transactions of the American Fisheries Society, vol. 131, no. 4, pp. 690–697.

Hill, R.D., 1974. Mining impacts on trout habitat. In: Proceedings of a Symposium on Trout Habitat, Research, and Management. Appalachian Consortium Press, Boone, NC.

Howells, G.D., Brown, D.J.A., and Sadler, K., 1983. Effects of acidity, calcium, and aluminum on fish

survival and productivity: a review. Journal of the Science of Food and Agriculture, vol. 34, no. 6, pp. 559–570.

Jennings, S.R., Neuman, D.R., and Blicker, P.S., 2008. Acid Mine Drainage and Effects on Fish Health and Ecology: A Review. Reclamation Research Group Publication, Bozeman, MT, 29 pp.

Johnson, D.W., Simonin, H.A., Colquhoun, J.R., and Flack, F.M., 1987. In situ toxicity tests of fishes in acid waters. Biogeochemistry, vol. 3, no. 1–3, pp. 181–208.

Kaeser, A.J., and Sharpe, W.E., 2001. The influence of acidic runoff episodes on slimy sculpin reproduction in Stone Run. Transactions of the American Fisheries Society, vol. 130, no. 6, pp. 1106–1115.

Kimmel, W.G., 1983. The impact of acid mine drainage on the stream ecosystem. In: Pennsylvania Coal: Resources, Technology, and Utilization, S.K. Majumdar and E.W. Willard, eds. Pennsylvania Academy of Science, Bradford, PA, pp. 424–437.

Maret, T.R., and MacCoy, D.E., 2002. Fish assemblages and environmental variables associated with hard-rock mining in the Coeur d'Alene River Basin, Idaho. Transactions of the American Fisheries Society, vol. 131, no. 5, pp. 865–884.

Martin, A.J., and Goldblatt, R., 2007. Speciation, behavior, and bioavailability of copper downstream of a mine-impacted lake. Environmental Toxicology and Chemistry, vol. 26, no. 12, pp. 2594–2603.

McCoy, J., 2010. Acid mine drainage kills fish in Kanawha Creek. Charleston Gazette, West Virginia. http://www.allbusi ness.com/environment-natural-resources/pollution-monitoring/15193152–1.html.

MEND. 2001. Mining Environment Neutral Drainage Program. In: G.A. Tremblay and C.M. Hogan, eds. CANMET, Canada Centre for Mineral and Energy Technology.

Menendez, R., 1978. Effects of acid water on Shavers Fork: a case history. In: Surface Mining and Fish/Wildlife Needs in the Eastern United States. FWS:OBS 78:81. U.S. Department of the Interior, Fish and Wildlife Service, Washington, DC, pp. 160–169.

Neuman, D.R., Brown, P., Jackson, D., and Jennings, S.R., 2009. Metals: Freshwater Fish Health and Ecology, A Literature Review. Reclamation Research Group Publication, Bozeman, MT, p. 73.

Olsen, J.B., Miller, S.J., Spearman, W.J., and Wenburg, J.K., 2004a. Patterns of Genetic Diversity in Alaskan Coho Salmon. Technical Report 5. North Pacific Anadromous Fish Commission, Vancouver, BC, Canada, pp. 55–57.

Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., and Blowes, D.W., 2000. Negative pH and extremely acidic mine waters from Iron Mountain, California. Environmental Science and Technology, vol. 34, no. 2, pp. 254–258.

Olsen, J.B., Miller, S.J., Harper, K., Nagler, J.J., Van Hatten, K., Whitton, K., and Wenburg, J.K., 2004b. Sex Ratios of Juvenile and Adult Chinook Salmon in the Kuskokwim and Yukon Rivers. Final Report for Study 02-097. Fisheries Resource Monitoring Program, Office of Subsistence Management, U.S. Fish and Wildlife Service, Anchorage, AK.

Price, W.A., 2005. List of Potential Information Requirements in Metal Leaching/Acid Rock Drainage Assessment and Mitigation Work. MEND, Canada Centre for Mineral and Energy Technology, Ottawa,

ON, Canada.

Schmidt, T.S., Soucek, D.J., and Cherry, D.S., 2002. Modification of an ecotoxicological rating to bioassess small acid mine drainage--impacted watersheds exclusive of benthic macroinvertebrate analysis. Environmental Toxicology and Chemistry, vol. 21, no. 5, pp. 1091–1097.

Soucek, D.J., Cherry, D.S., Currie, R.J., Latimer, H.A., and Trent, G.C., 2000. Laboratory and field validation in an integrative assessment of an acid mine drainage–impacted watershed. Environmental Toxicology and Chemistry, vol. 19, no. 4, pp. 1036–1043.

U.S. Department of Agriculture, 1993. Acid Mine Drainage from Impact of Hard Rock Mining on the National Forests: A Management Challenge. USDA Forest Service, Program Aid 1505:12. USDA, Washington, DC.

U.S. Environmental Protection Agency (EPA), 1995. Human Health and Environmental Damages from Mining and Mineral Processing Wastes. Office of Solid Waste, U.S. EPA, Washington, DC.

U.S. Environmental Protection Agency, 2000. 40 CFR Part 300 [FRL-6603–3], Federal Register Notice. Leviathan Mine, Alpine County, California, vol. 65, no. 92/30482–30488; Thursday, May 11, 2000/Rules and Regulations. http://www.epa.gov/superfund/sites/npl/nar1580.htm.

U.S. Environmental Protection Agency, 2010. Region 9 Superfund Iron Mountain Mine. EPA CAD980498612. Site Documentation. http://yosemite.epa.gov/R9/SFUND/R9SFDOCW.NSF/VIEWBYEPAID/CAD980498612?OPENDOCUMENT.

Warner, R.W., 1971. Distribution of biota in a stream polluted by acid mine drainage. Ohio Journal of Science, vol. 71, no. 4, pp. 202–215.

Woodward, D.F., Goldstein, J.K., Farag, A.M., and Brunbaugh, W.G., 1997. Cutthroat trout avoidance of metals and conditions characteristic of a mining waste site: Coeur d'Alene River, Idaho. Transactions of the American Fisheries Society, vol. 126, no. 4, pp. 699–706.

13
Metals Associated with Acid Rock Drainage and Their Effect on Fish Health and Ecosystems

DENNIS R. NEUMAN, PETER J. BROWN, AND STUART R. JENNINGS

The release of sulfuric acid and a variety of metals into freshwater ecosystems as part of the acid generation process associated with resource extraction activities affects freshwater fish health and other aquatic organisms. In this chapter we examine metals in the environment and trace metal assimilation by aquatic organisms in three parts: (1) a general description of the physical and chemical factors that control the behavior of metals that have been associated with acid rock drainage, (2) detailed descriptions of selected metals most frequently associated with acid rock drainage, and (3) the uptake of these metals by fish and other aquatic organisms (Neuman et al., 2009).

Introduction

There are 90 naturally occurring elements in Earth's environment. These elements are generally divided into metals, nonmetals, and metalloids. Metals are characterized by high electrical conductivity due to their atoms' ability to lose electrons, thereby forming positively charged ions. Metals tend to react with oxygen; for example, iron and oxygen form common rust. Metals in general have high electric, thermal conductivity, luster, and density. The metalloids or semimetals are located along the line between the metals and the nonmetals in the periodic table. The metalloids are boron, silicon, germanium, arsenic, antimony, and tellurium. These elements display both metal and nonmetal properties. From an environmental perspective, metalloids are sometimes grouped with metals.

Metals are ubiquitous and a natural part of Earth's environment. All living organisms contain metals, and trace amounts are found in seawater, dust, and in the atmosphere. Some metals can be found in nature in their elemental state, such as gold, silver, and copper; however, most metals are found in nature as minerals, which are crystalline combinations of elements. Concentrations of metals in Earth's lithosphere, soils, air, water, and biological organisms are described in textbooks and government publications (e.g., Pais and Jones, 1997; Adriano, 2001; Kabata-Pendias, 2001). Two terms are often seen in the scientific literature: heavy metals and trace metals. *Heavy metals* are metals with densities greater than that of iron and include elements of ecological and human concern, such as mercury, lead, and cadmium. The term sometimes includes all metal elements of environmental concern. The term *trace element* implies that the concentration of the element in natural media is less than 0.1% (Adriano, 2001). In biochemical research, trace elements are usually present in plants or animals in concentrations below 0.01% of the organism (Adriano, 2001). Elements required only in small quantities by living organisms are termed *trace elements*, *microelements*, or *micronutrients*.

Natural Sources of Metals

Rocks are the natural source of metals in the environment. Several processes are involved in the mobilization, dispersion, deposition and distribution, and eventual concentration of metals in ecosystems. These processes are physical, chemical, and biological and include weathering, decomposition,

dissolution, oxidation–reduction, bacterial influences, and others. The atmosphere contains metals as particulates, aerosols, and gases. Sources include geothermal geysers, forest fires, and volcanoes, and volatilization. These metals can be deposited in surface water by dry deposition or precipitation. The physical state of metals, solid phase or in solution, in soils and sediments can affect their mobility (how likely they are to move in the environment) and bioavailability (how likely they are to be assimilated into biological organisms) (Adriano, 2001; National Research Council, 2005).

Rocks are classified into three groups according to the major earth processes that formed them: igneous, sedimentary, and metamorphic. *Igneous rocks* are formed from melted rock that has cooled and solidified. *Sedimentary rocks* are formed at the surface of the Earth, either in water or on land. They are layered accumulations of sediments: fragments of rocks, minerals, and animal or plant material. *Metamorphic rocks* are formed under the surface of the Earth due to high temperatures and pressures. Igneous rocks are a major source of metals held in minerals (Siegel, 2002). Decomposition via weathering of the minerals by air and water releases both soluble and insoluble metals. Bacteria can play a role in the dissolution of metals and their subsequent release into the surrounding environment. Sedimentary rocks are also sources of metals, as particles and sediments are eroded by water and wind and sediments are transported to surface waters. Metamorphic rocks can also contain metal-bearing minerals. Natural concentrations of metals in surface water and groundwater are controlled by the chemical composition of soils and rocks over which or through which the water flows. The chemistry of the metals in these waters is dependent on several chemical, physical, and biological attributes. Waters flowing through or over pyritic minerals are expected to be of elevated acidity (low pH), whereas waters emanating from limestone outcrops are expected to be alkaline, with pH values near 8.3 (Siegel, 2002). The behavior of metals and the environmental consequences in these two situations are different because pH is a major factor controlling metal solubility.

Metal Transport and Cycling

Factors Affecting Metal Behavior in Soils

The most important regulators of metal behavior are pH, oxidation–reduction reactions, and cation-exchange capacity. Of these, pH—a measure of hydrogen-ion activity of a solution—is the master driver (Adriano, 2001). Because hydrogen ions carry a single positive charge, they influence reactions, including precipitation and dissolution of metals and redox reactions. Mobility, leaching, and bioavailability of metals are affected by pH as exhibited in Figure 13.1. In general, low pH (high concentration of hydrogen ions) increases metal solubility, because the hydrogen ions compete with other positively charged ions for available exchange sites on minerals or soils. Therefore, low pH increases the mobility and bioavailability of most positively charged (cationic) metals; exceptions to this general rule include molybdenum, vanadium, chromium, and the metalloids arsenic and selenium. In high-pH environments, most metals become less mobile and bioavailable, due to precipitation and complexation with negatively charged oxides and oxyhydroxides.

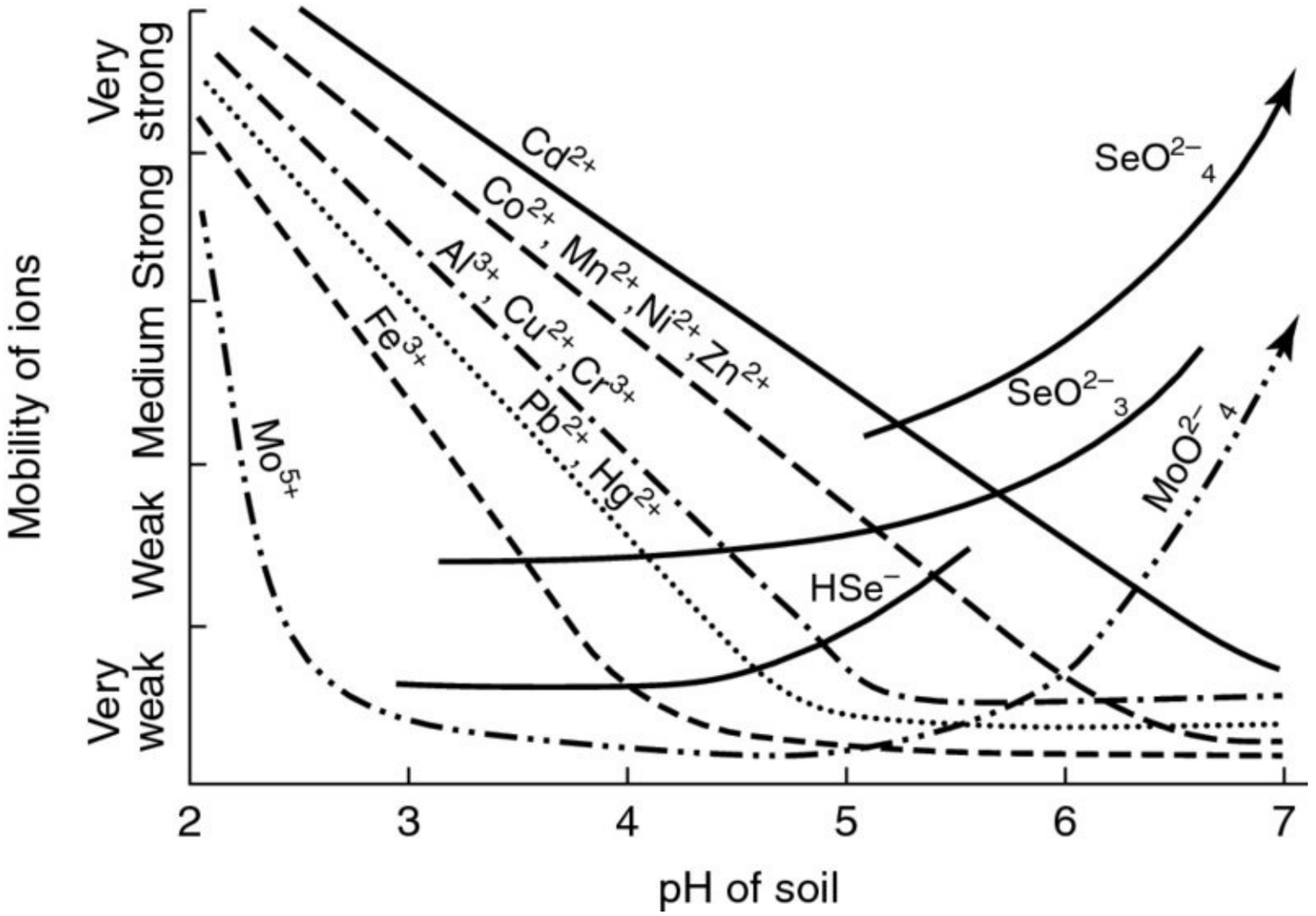


FIGURE 13.1 Influence of pH on the mobility of metal ions and some anions. (From Kabata-Pendias, 2001.)

Metals are characterized by their ability to lose electrons, thereby becoming positively charged ions. This process is termed *oxidation–reduction*, or *redox*. When a metal atom loses electrons (becoming more positive), it is oxidized, while the atom or molecule that gains the electron (becoming more negative) is reduced. This shift of electrons between atoms is a fundamental chemical process. A common redox reaction is the oxidation of iron to form rust. In this chemical reaction, iron atoms lose three electrons, becoming Fe^{3+}, while oxygen sequesters them. The resulting molecule is iron oxide (Fe_2O_3). Other metals can be oxidized when exposed to oxygen, resulting in positive ions that are often soluble in aquatic environments (Pagenkopf et al., 1974). Relationships among pH, oxidation–reduction potential or redox (Eh), environmental changes, and metal mobility are represented in Figure 13.2.

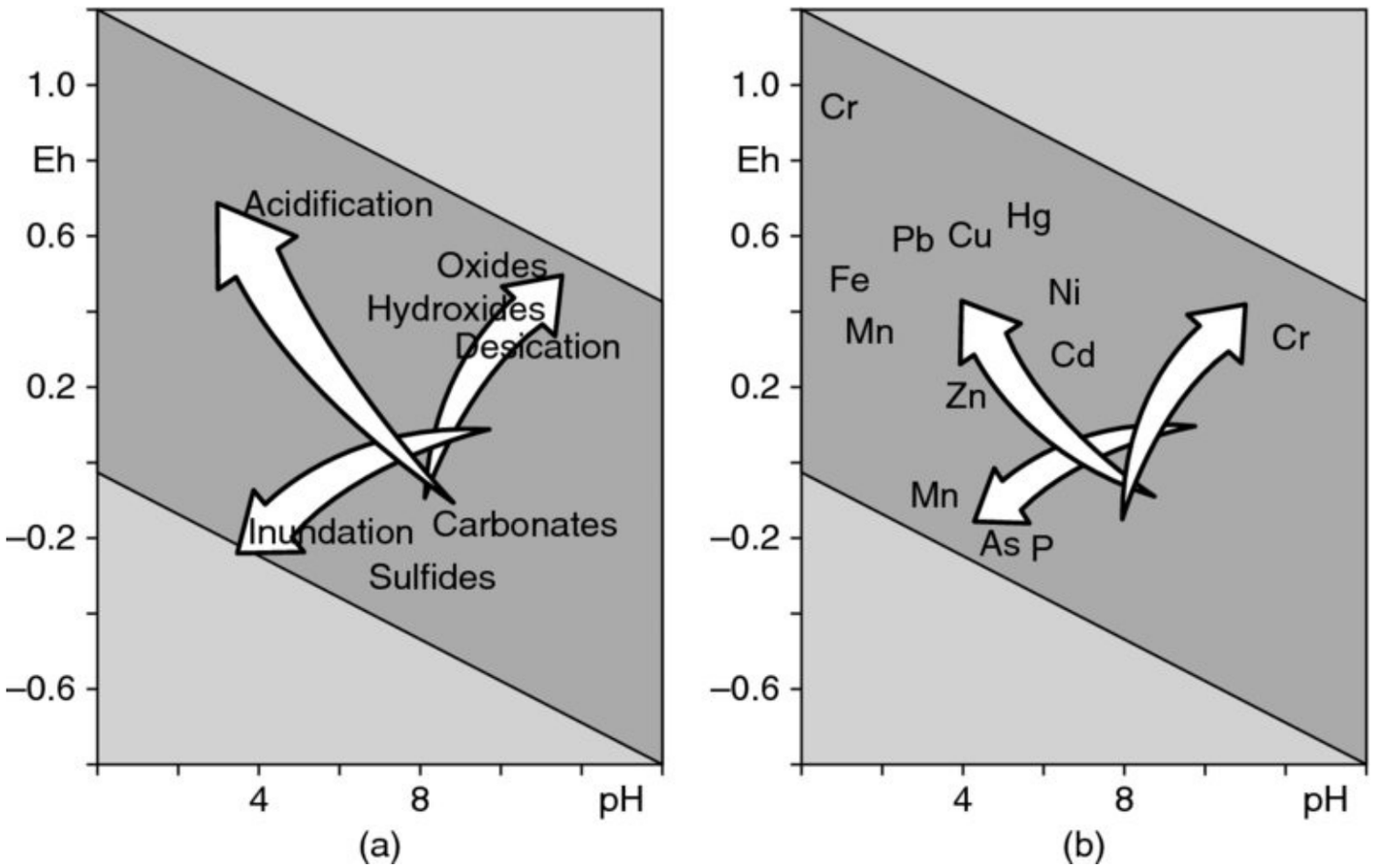


FIGURE 13.2 Relationships between pH and Eh: (a) environmental changes; (b) resulting metal mobility and form. (From Seigel, 2002.)

Under low-pH conditions and oxidation (positive Eh value) conditions, acidification is favored, as indicated in Figure 13.2a. Acid conditions tend to make most metals more mobile and bioavailable, as indicated in part b. Metals tend to precipitate as oxides and hydroxides under elevated pH/positive Eh conditions. Negative Eh values indicate a reducing environment, and most metals form sulfides under these conditions and mobility is limited.

Valence electrons of metals, those in the outermost orbital shells, determine how metal atoms lose, gain, and share these electrons with other elements. Valence electrons define four basic metal properties that influence behavior: electronegativity, oxidation state, ionic radius, and ionic potential. *Electronegativity* is the tendency of an atom to lose or gain electrons in the outer orbits; elements with high electronegativity have a tendency to gain electrons and those with low electronegativity easily lose electrons). Most metals have low electronegativity and are therefore easily ionized into a positively charged form. Electronegativity therefore dictates the type of chemical reactions and chemical bonds that certain metals will form. *Oxidation state* is the charge that an atom has when electrons are counted and determines how electrons are allocated between atoms in oxidation–reduction reactions. *Ionic radii* relate to the size and shape of an element and are related to the oxidation state. Several metals (e.g., iron and copper) can exist in different oxidation states, and therefore can take part in multiple redox reactions. *Ionic potential* is a measure of the ratio of oxidation number to ionic radius. Elements with similar ratios can sometimes substitute for each other in biological systems. Ionic potential partially explains how elements that seem chemically different can act similarly in the environment. For example, the anions phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) are similar, and organisms can assimilate arsenic by using an active transport system normally used in phosphate transport (Eisler, 1988).

Other important soil factors in controlling metal movement are exchange sites (clays, which have negatively charged exchange sites, tend to decrease metal mobility) and organic matter, which can form metal complexes. How a metal is bound to the soil is also an important factor in its mobility and bioavailability. Determinations of the total concentrations of metals in soils may not be representative of the concentration that is bioavailable or a threat to the environment. Individual metals may be bound to a soil in different solid phases as easily soluble, bound to exchange sites, complexed with iron and manganese oxy/hydroxides, or chelated with soil organic matter. Metals held tightly (i.e., residual within a crystalline lattice) are not easily solubilized under environmental conditions. Individual metals are held in different solid phases, as depicted in Figure 13.3.

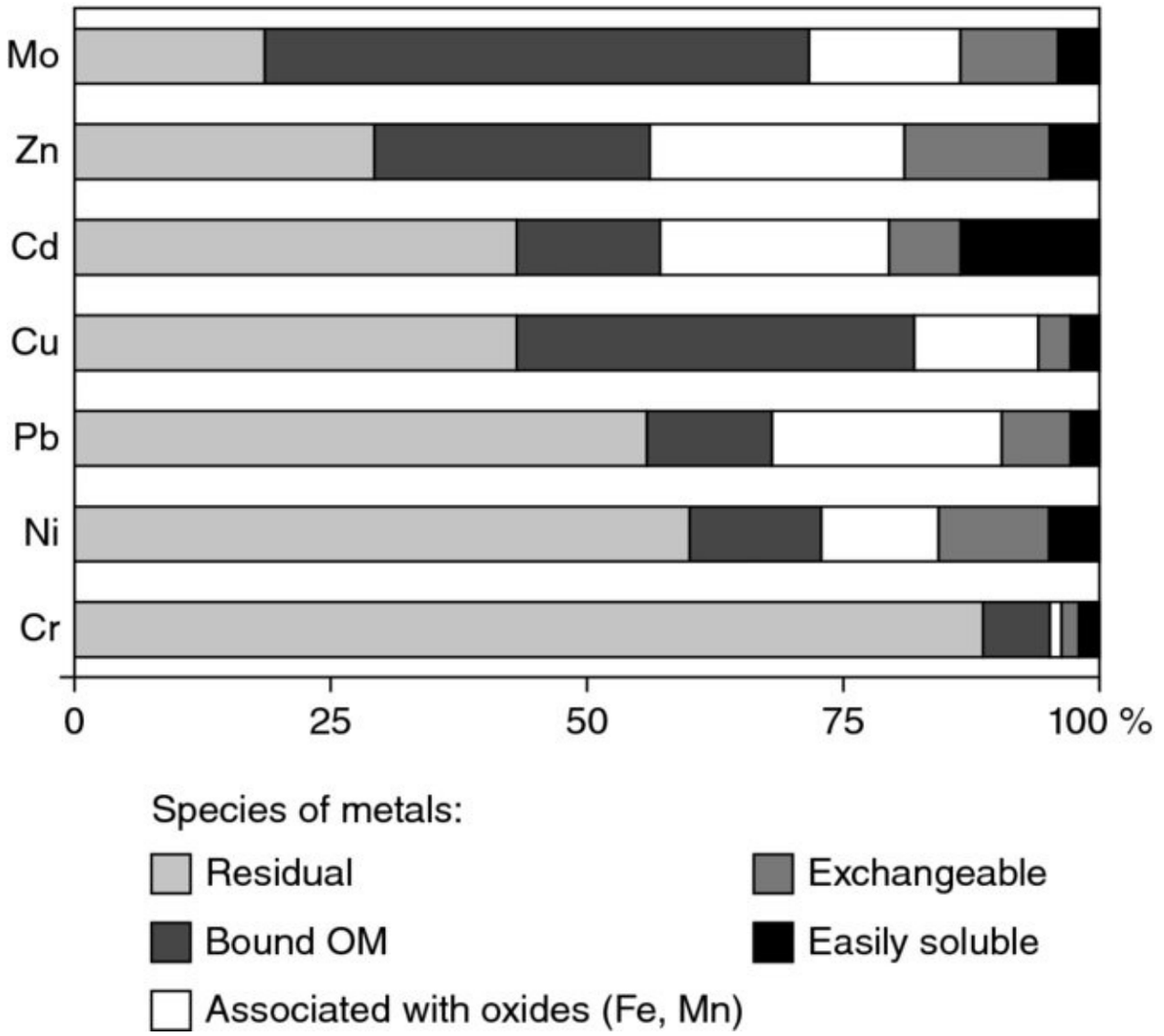


FIGURE 13.3 Distribution of metals in solid phases in soils. (From Kabata-Pendias, 1993.)

Factors Affecting Metal Behavior in Fresh Water

In freshwater systems, metal mobility and transport are controlled by the following processes: (1) aerial deposition of acidic and neutralizing compounds; (2) weathering—both mobilization and neutralization; (3) dilution from runoff and concentration from evaporation; (4) recharge from groundwaters and detention; and (5) buffering and geochemical reactions occurring in streams and lakes (Hart, 1982; Salomons and Forstner, 1984). Humic substances are important in aquatic environments and may represent 70 to 90% of dissolved organic carbon in wetland waters (Thurman, 1985). Humic substances are the dark organic component of soils. They are heterogeneous mixtures of small molecules that arise

from the biological transformation of dead plant and animal cells. These humic molecules tend to bind or chelate (form a metal organic compound) metals and control metal species, which in turn affect their mobility, bioavailability, and toxicity (Florence and Batley, 1980).

Temporal and Spatial Variability of Metals in Aquatic Environments

Trace metals can enter aquatic food webs from one of two sources: sediment or water. Of the total load in a stream, 90 to 99% can be in the sediment (Graf et al., 1991). But often these sediments are not associated with flowing water and therefore release associated metals only slowly (Miller, 1997). Metals dissolved in surface water can be higher in concentration than those that are bioaccumulated (Farag et al., 2003). Concentrations in the water can fluctuate hourly, whereas metals in the sediment can persist for decades. Trace metals in fluvial sediments are usually associated with 2-mm or smaller particles (Graf et al., 1991). These sediments can vary spatially because of the hydraulic sorting processes associated with turbulent currents (Ladd et al., 1998). Metal-bound sediments can be found in areas of low velocity where fine particles are deposited. Shifting channels cover the sediments through depositional processes, incorporating them into the riparian alluvium. The deposition patterns of metal sediments are complex vertically and laterally due to geomorphologic processes (Miller, 1997). Sediments can remain for tens or hundreds of years and can affect riparian plant growth (e.g., white poplar; Madejon et al., 2004). The effect of tributaries should also be considered in trace metal concentration of rivers. Tributaries not only have a diluting effect on total concentration but also allow areas of even lower metal concentration around their mouth. Along with the tributary itself, these areas can act as refugia for aquatic organisms (Axtmann et al., 1997).

Trace metal concentrations in the aqueous environment vary temporally. Metal concentration can change in diel (daily) and/or seasonal cycles, or pulses can be random (e.g., related to rain events; Meylan et al., 2003; Nimick et al., 2005). Diel cycles in aqueous metal concentrations have been documented widely. The cause of these cycles has been attributed to geochemical, biochemical, and hydrological events (reviewed by Nimick et al., 2005). Light mediates the concentration of zinc in streams (Morris et al., 2006), suggesting that the cause of the cycle is related to adsorption and desorption associated with photosynthesis (Jones et al., 2004). However, Nimick et al. (2005) observed diel (24-h) metal concentrations that arsenic exhibited a cycle opposite that of other metals, such as manganese and zinc, and suggested that the cause of the cycle may be metal-specific and that geochemical raher than hydrological processes are the primary control of the diel metal concentration cycles. Seasonal cycles can be associated with snowmelt or photosynthesis, and it is important to recognize these cycles when sampling metals in surface waters (Nimick et al., 2005).

Chemical Speciation in Soils and Waters

Chemical speciation, the form of the element or metal, is important in assessing the mobility, bioavailability, and potential toxicity to organisms. Dominant chemical forms of the priority metal pollutants and the form or species considered to be most toxic are provided in Table 13.1.

Table 13.1 Some Chemical Species of Metals and Their Potential Toxicity to Organisms

	Dominant Chemical Species		
Priority	**Soil**	**Water**	**Most Toxic**
Antimony	SbO_x	$Sb(OH)_6^{2-}$	?
Arsenic	AsO_4^{3-}	AsO_4^{3-}; AsO_3^{3-}	AsO_4^{3-}
Beryllium	Be^{2+}; $Be_xO^{2x-2y}{}_y$	Be^{2+}	Be^{2+}
Cadmium	Cd^{2+}	Cd^{2+}	Cd^{2+}
Chromium	Cr^{3+}	Cr^{3+}; Cr^{6+}	Cr^{6+}
Copper	Cu^{2+}	Cu^{2+}-fulvate	Cu^{2+}
Lead	Pb^{2+}	$Pb(OH)^+$	Pb^{2+}
Mercury	Hg^{2+}; Hg^{2+}-fulvate	CH_3Hg; $HgCl_2$; $Hg(OH)_2$	CH_3Hg
Nickel	Ni^{2+}	Ni^{2+}	Ni^{2+}
Selenium	$HSeO_3^-$ SeO_4^{2-}	SeO_4^{2-}	SeO_4^{2-}
Silver	Ag^+	Ag^+	Ag^+
Thallium	?	?	?
Zinc	Zn^{2+}	Zn^{2+}	Zn2+

Source: Adapted from Logan and Traina (1993) as cited in Adriano (2001).

Essentiality

Essential elements for vertebrates include calcium, chlorine, chromium, cobalt, copper, fluorine, iodine, iron, magnesium, manganese, molybdenum, phosphorus, potassium, selenium, sodium, sulfur, and zinc (National Research Council, 2005). Life requires that some metals be present within certain concentration ranges and in combinations with other elements. Concentrations of metals that are too low can result in nutrient deficiencies; metal concentrations that are too high can be phytotoxic to plants and toxic to animals and humans (Table 13.2). Essential elements (metals and metalloids) have well-defined biochemical roles, such as activating proteins, including enzymes; maintaining pH and ionic balance; and providing structural integrity and metabolic signals for homeostasis. Some metals serve important roles in enzymes. Metalloenzymes are involved in the synthesis, repair, and degradation of biological molecules. They are also involved in biological signaling processes and in the transfer of electrons and small molecules in photosynthesis and respiration. Six additional elements that might provide beneficial effects when added to animal diets include arsenic, boron, nickel, rubidium, silicon, and vanadium (Adriano, 2001). The list of essential or beneficial elements for plants is slightly different.

Table 13.2 Classification of Some Trace Elements as Plant and Animal Nutrients or Toxins

Trace Element	Essential to Plants?	Essential to Animals?	Toxic to Plants?	Toxic to Animals?
Arsenic	No	Yes	Yes	Yes
Boron	Yes	No	Yes	Unknown
Cadmium	No	No	Yes	Yes
Chromium	No	Yes	Yes	Yes[a]
Cobalt	Yes	Yes	Yes	Yes
Copper	Yes	Yes	Yes	Yes
Lead	No	No	Yes	Yes
Manganese	Yes	Yes	Yes	Yes
Mercury	No	No	Yes	Yes
Molybdenum	Yes	Yes	Yes	Yes
Nickel	Yes	Yes	Yes	Yes
Selenium	No	Yes	Yes	Yes
Vanadium	Yes	Maybe	Yes	Yes
Zinc	Yes	Yes	Yes	Yes

Source: Based on Adriano (1986), Kabata-Pendias (2001), and Smith and Huyck (1999).

[a] Cr^{6+} oxidation state.

It is noted that consensus among scientists with regard to elements that are essential, nonessential, and perhaps beneficial is not universal (Pais and Jones, 1997). As early as 1939, Arnon and Stout defined requirements for element essentiality for plants as follows: (1) the organism can neither grow nor complete its life cycle in the absence of the element; (2) the element cannot be replaced completely by any other element; and (3) the element has a direct influence on the organism and is involved in its metabolism. Twenty-five years later, Hewitt and Smith (1974) considered an element essential for plants if it met the following criteria: (1) omission of the element must directly cause abnormal growth or failure to complete the life cycle, or permanent senescence and death; (2) the effects must be specific, and no other element can be substituted in its place; and (3) the effect must be direct on some aspect of growth or metabolism. Indirect or secondary beneficial effects of an element, such as reversal of the inhibitory effect on some other element, disqualify the element as essential. At about the same time, Underwood (1977) suggested essentiality criteria for animals: (1) consistent significant growth response to dietary supplements of the element and this element alone, (2) development of the deficiency state when on diets otherwise adequate and satisfactory, and (3) correlation of the deficiency state with the occurrence of subnormal levels of the element in the blood or tissues of animals exhibiting the response.

Metals, regardless of essentiality or nonessentiality, can affect plants and animals adversely when concentrations become excessive, such as those associated with acid rock drainage. The range in concentration for a specific essential element can be quite narrow or broad and can depend on the species of plant or animal. It is generally thought that elements that were enriched in the aquatic environment of early evolution became essential and are tolerated at much higher levels than elements that are nonessential and were, in geological time, present in low concentrations (National Research Council,

2005). Protective mechanisms for maintaining equilibrium between sufficient and excessive concentrations of elements are part of this evolutionary process. These evolutionary mechanisms ensure that the transport, storage, and disposal of essential metals and the protective systems for nonessential metals are operative. Proteins called *metallothioneins* can complex toxic metals and inhibit them from interacting with other biological molecules. At a low concentration, a deficiency status may be prevalent; as the concentration increases, the organism experiences optimal growth or health, but at a still greater metal level a toxic response is reached (Figure 13.4a).

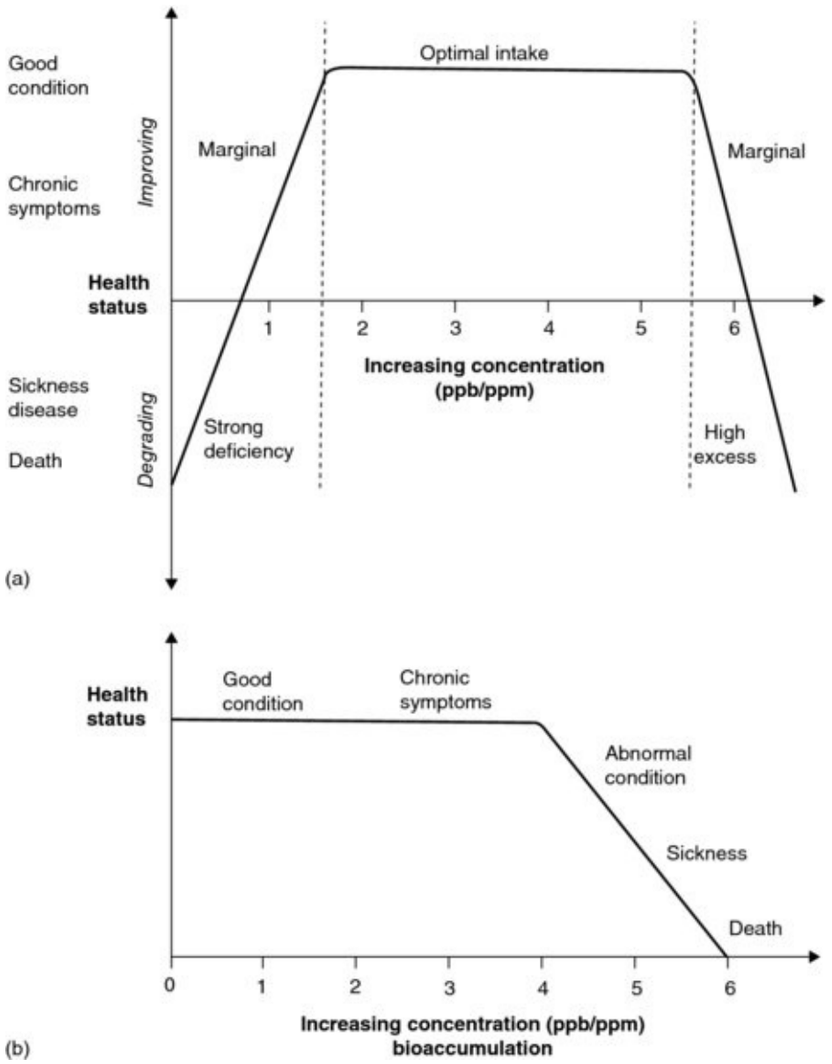


FIGURE 13.4 Relationship between organism growth or health and dietary concentration for an essential element (a) and a nonessential element (b). (From Siegel, 2002.)

Low concentrations are tolerated without adverse effect, but at some level, detrimental effects are exhibited and toxic conditions may be present at still even greater concentrations (Figure 13.4b). The toxic effects of most metals relate to their ability to interrupt the function of essential biological molecules, including enzymes, proteins, and DNA (National Research Council, 2005). In some cases, metals displace chemically similar metal ions. For example, the nonessential metal cadmium can under some circumstances replace the essential metal zinc, thereby interfering with certain proteins that require zinc for their structure and function (National Research Council, 2005).

Metal Priority Pollutants

The U.S. Environmental Protection Agency (EPA) has a major interest in, and has listed, the following

metals or metalloids as priority pollutants: antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc (40 CFR part 401.15). The EPA regulates these metals and has published analytical test methods for them. Some of them also play important biological roles and are considered to be essential for plants, animals, and humans.

Soil Concentrations of Priority Metal Pollutants

Most soils consist of various layers, soil horizons, which have different properties and concentrations of elements, including metals. These horizons may be quite thin, a few millimeters, or thick, several meters. Shacklette and Boerngen (1984) determined means and ranges in concentration within the top 20 cm of soils in the United Sates. For priority pollutant elements, these concentrations for soil in the western states are given in Table 13.3. Priority pollutant metal concentrations in groundwaters as reported by the U.S. Congress's Office of Technology Assessment (van der Leeden et al., 1990) are provided in Table 13.4. The U.S. Environmental Protection Agency (2009) has established national recommended water quality criteria for priority metal pollutants. Values for freshwater aquatic receptors are provided in Table 13.5.

Table 13.3 Mean and Range of Priority Pollutant Metals in Soils from the Western United States

Priority Pollutant	Mean Value[a]	Range (ppm)
Antimony	0.47	< 1 to 2.6
Arsenic	5.5	< 0.10 to 97
Beryllium	0.68	< 1 to 15
Cadmium[b]	0.18	0.1 to 5
Chromium	41	3 to 2000
Copper	21	2 to 300
Lead	17	< 10 to 700
Mercury	0.046	< 0.01 to 4.6
Nickel	15	< 5 to 700
Selenium	0.23	< 0.1 to 4.3
Silver[b]	0.07	0.02 to 0.1
Thallium[b]	1	0.1 to 3
Zinc	55	10 to 2100

Source: Adapted from Shacklette and Boerngen (1984).

[a]Geometric mean value or approximate consensus value.

[b]Earth crust abundance, adapted from Rickwood (1983).

Table 13.4 Concentration Range of Priority Pollutant Metals in Groundwaters Within the United States

Priority Pollutant	Range (µg/L)
Antimony	-
Arsenic	0.01 to 2100
Beryllium	<0.01
Cadmium	0.01 to 180
Chromium	0.06 to 2740
Copper	0.01 to 2.8
Lead	0.01 to 5.6
Mercury	0.003 to 0.01
Nickel	0.05 to 0.5
Selenium	0.6 to 20
Silver	9.0 to 330
Thallium	-
Zinc	0.1 to 240

Source: U.S. Congress's Office of Technology Assessment figures (1984) as cited in van der Leeden et al. (1990).

Table 13.5 National Recommended Water Quality Criteria for Priority Pollutant Metals

Priority Pollutant	Criteria Maximum Freshwater Concentration[a] (Acute) (µg/L)	Criterion Continuous Freshwater Concentration[a] (Chronic) (µg/L)
Antimony	NVE[b]	NVE
Arsenic	340	150
Beryllium	NVE	NVE
Cadmium	2.0	0.25
Chromium (III)	570	74
Chromium (VI)	16	11
Copper	13	9.0
Lead	65	2.5
Mercury	1.4	0.77
Nickel	470	52
Selenium	NVE	5.0
Silver	3.2	NVE
Thallium	NVE	NVE
Zinc	120	120

Source: U.S. Environmental Protection Agency (2009).

[a]The *criteria maximum concentration* (CMC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect. The *criterion continuous concentration* (CCC) is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect. The CMC and CCC are just two of the six parts of an aquatic life criterion; the other four parts are the acute averaging period, chronic averaging period, acute frequency of allowed exceedance, and chronic frequency of allowed exceedance. Because the 304(a) aquatic life criteria are national guidance values, they are intended to be protective of the vast majority of the aquatic communities in the United States.

[b]NVE, no value established.

The National Oceanic and Atmospheric Administration published a series of screening quick reference tables (SQuiRTs). This handy reference tool presents screening concentrations for inorganic and organic contaminants in various environmental media. The SQuiRT tables, which were developed for preliminary screening, are helpful in evaluating the potential risk from contaminated water, sediment, or soil. Data selected from these tables are presented in Table 13.6 for priority metals in soils, sediments, and waters. For a complete description of the SQuiRTs, see http://response.restoration.noaa.gov/index.php.

Table 13.6 Benchmark Concentrations for Selected Metals and Metalloids in Soils, Freshwater Sediments, and Fresh Waters

Matrix	As	Be	Cd	Cr	Cu	Hg	Mn	Pb	Ni	Ag	Sb	Se	Tl	Zn
Soils (ppm)														
Background[a]	5.2	0.63	—	<37	17	0.058	330	16	13	—	0.48	0.26	8.6	48

Range	bd–97	bd–15	—	—	bd–700	bd–4.6	bd–0.7%	bd–700	bd–700	—	bd–8.8	bd–4.3	0.22–3 1	bd–0.3%
Target[b]	0.9	1.1	0.8	0.38	3.4	0.3	—	55	0.26	—	3	0.7	1	16
Intervention[b]	55	30	12	220	96	10	—	530	100	15	15	100	15	350
ECO-SSL[c]														
Avian	43	—	0.77	—	28	—	4300	11	210	4.2	—	1.2	—	46
Invertebrates	60	40	20	<0.4	50	0.10	450	500	200	—	78	4.1	—	6.6
Mammals	5.7	1.0	0.002	81	5.4	—	4000	0.054	13.6	4.0	0.143	0.63	0.57	—
Plants	18	10	4	<1	70	0.3	220	50	30	2	5	0.52	1	50
Microbes	100	—	20	<10	100	30	100	900	90	50	—	100	—	100
Freshwater														
Sediments														
BackGround[d]	1.1	—	0.1–0.3	7–13	10–25	0.004–0.051	400	4–17	9.9	<0.5	160	290	—	7–38
LEL[e]	6.0	—	0.6	26	16	0.2	460	31	16	>500		—	—	120
SEL[e]	33	—	10	110	110	2.0	1100	250	75	—		—	—	820
Waters (ppb)														
Groundwater[f]	10	4	5	100	1300	2	50	15	20	100	6	50	2	5000
Acute[g]	340	35	2.0[h]	—	13[h]	1.4	2300	65[h]	470[h]	1.6[h]	88	13–186	10	120[h]
Chronic[g]	150	0.66	0.25[h]	—	9[h]	0.77	80	2.5[h]	53[h]	—	30	5	—	1208[h]

Source: Data are adapted from http://response.restoration.noaa.gov/book shelf/122 NEW-SQuiRT s.pdf.

[a]Shacklette and Boerngen (1984).

[b]E.M.J., Verbruggen, R. Posthumus, and A.P. van Wezel, 2001, Dutch Target/Intervention: Ecotoxicological Risk Concentrations in Soils, Sediments, and (Ground)water, National Institute of Public Health and the Environment, Washington, DC.

[c]U.S. EPA, Ecological Soils Screening Levels (ECO-SSL), Office of Solid Waste and Emergency Response, Washington, DC, http://www.epa.gov/ecotox/ecossl/.

[d]M. Buchman, NOAA HAZMAT Report 99-1.

[e]These benchmarks are based on chronic, long-term impacts of contamination to benthic organisms. The lowest effect level (LEL) is a level of sediment contamination that can be tolerated by the majority of benthic organisms. The severe effect level (SEL) is that at which pronounced disturbance of the sediment-dwelling community can be expected. This is the concentration that would be detrimental to the majority of the benthic community.

[f]U.S. EPA, Maximum Contaminant Levels (MCLs), http://epa.gov/safewater/index.html.

[g]U.S. EPA. Ambient Water Quality Criteria (AWQC), http://epa.gov/waterscience/criteria/aqlife.html.

[h]These concentrations are hardness dependent. See http://response.restoration.noaa.gov/book_shelf/122_NEW-SQuiRTs.pdf for calculation

formulas.

Metals Associated with ARD of Interest to Freshwater Fish Health and Ecology

Arsenic

Arsenic is a relatively common element that occurs in air, water, soil, and all living tissues. It ranks twentieth in abundance in the Earth's crust, fourteenth in seawater, and twelfth in the human body. Arsenic is ubiquitous in the environment and commonly associated with acid rock drainage. It is released into the air by volcanoes, through weathering of arsenic-containing minerals and ores, and by commercial or industrial processes. In industry, arsenic is a by-product of the smelting process for many metal ores. Elevated arsenic soil concentrations are often associated with mining activities, smelters, pesticide and herbicide manufacturing facilities, and agricultural lands (American Petroleum Institute, 1998).

Although arsenic is carcinogenic in humans, evidence for arsenic-induced carcinogenicity in other mammals is scarce. Paradoxically, evidence is accumulating that arsenic is nutritionally essential or beneficial in very low concentrations (National Research Council, 2005). Arsenic-deficiency effects, such as poor growth, reduced survival, and inhibited reproduction, have been recorded in mammals fed diets containing less than 0.05 mg As/kg, but not in those fed diets with 0.35 mg As/kg. At comparatively low doses, arsenic stimulates growth and development in various species of plants and animals (Eisler, 1988).

Arsenic exists in four oxidation states, as inorganic or organic forms. Its bioavailability and toxic properties are modified significantly by biotic and abiotic factors, including the physical and chemical forms of arsenic, the route of administration, the dose, and the species of animal. In general, inorganic arsenic compounds are more toxic than organic compounds, and trivalent species are more toxic than pentavalent species. Arsenic may be absorbed by ingestion, inhalation, or through permeation of skin or mucous membranes; cells take up arsenic through an active transport system normally used for phosphate. The Geophysical Institute at the University of Alaska–Fairbanks cited the potential of this phenomenon in the following case history.

Case Study: Arsenate and Phosphate: Chemical Look-alikes

The finding of a high arsenic content in some wells located near gold-bearing deposits in the Fairbanks mining district has created special concern because of possible health problems. Arsenic can cause skin and mucous membrane cancer and can damage small blood vessels, thereby leading to heart disease, kidney failure, brain damage, and decreased tolerance to cold. Young people seem to be affected more than the elderly.

An arsenic atom will readily combine with four oxygen atoms to form on arsenate molecule. The arsenate molecule is a chemical look-alike to the phosphate molecule, formed similarly from phosphorus and oxygen. Phosphorus is an important element for living organisms. It forms nerve tissue, bones, and teeth. Also, it makes up a part of the membrane tissue that surrounds living cells and transports the energy that fuels muscle contraction.

The cells recognize the shape of the phosphate molecule and readily absorb it. Unfortunately, the shape of arsenate is so nearly identical that cells do not distinguish between arsenate and phosphate. Thus, if substantial concentrations of arsenate are provided to the body, the damaging arsenate is taken into cells instead of the phosphate which the cells need. This substitution of the bad for the good perhaps explains

why arsenic poisoning can retain its latency over the years, especially in children since their bodies are rapidly growing.

Button, D, and T.N. Davis. 1997. Arsenate and phosphate – chemical look-alikes, Article #168. Alaska Science Center, Geophysical Institute, University of Alaska, Fairbanks.

The mechanisms of arsenic toxicity differ greatly among chemical species, although all appear to cause similar signs of poisoning. Methylation is the preferred detoxification mechanism for absorbed inorganic arsenicals; methylated arsenicals usually clear from tissues within a few days (National Research Council, 2005). The relative mobility of arsenic in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH are as shown in Table 13.7.

Table 13.7

Redox Condition	System pH	Relative Mobility of Arsenic
Oxidizing	< 3	Mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Scarcely mobile to immobile
Reducing, no H_2S	> 5 to neutral	Somewhat mobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Antimony

Antimony is a silvery light, brittle metal and is usually mixed with other metals, such as lead and zinc, as alloys and is used in a wide variety of applications in the industrial processes. Antimony is a metalloid and can exist as either a cation or an anion. Oxidation states include Sb^{3+} and Sb^{5+}. It is a nonessential element, and the mean concentration in soils is 0.9 mg/kg (range 0.01 to 1.0 mg/kg) (Pais and Jones, 1997). Freshwater levels are generally less than 2 µ/L, and the most common species in water is $Sb(OH)^{6-}$ (Pais and Jones, 1997). According to the Agency for Toxic Substances and Disease Registry (ATSDR), antimony enters the environment during the mining and processing of its ores and in the production of antimony metal, alloys, antimony oxide, and combinations of antimony with other substances. Little or no antimony is mined in the United States. Antimony ore and impure metals are brought into this country for processing from other countries (http://www.atsdr.cdc.gov/toxprofiles/phs23.html).

ATSDR's Toxicology Profile reports that the concentration of antimony dissolved in rivers and lakes is about 5 µg/L. Antimony does not appear to accumulate in fish and other aquatic animals. The concentration of antimony dissolved in one polluted river where wastes from antimony mining and processing had been dumped was as high as 8 µg/L (Wilson et al., 2004). The cause of seabird killing in the Irish Sea in 1969 was unknown but suspected to be industrial waste dumping in the ocean. Livers of the dead birds were reported (Holdgate, 1971) to contain high levels of antimony, ranging from 40 to 400 ppm. The report did not assign antimony as the causative factor in the birds deaths, but Tucker (1972) stated that 400 ppm could be considered a lethal threshold for these birds.

Antimony does not appear to bioconcentrate appreciably in fish and aquatic organisms. No detectable bioconcentration occurred during a 28-day test in bluegills (U.S. Environmental Protection Agency, 1980). Only low levels of antimony have been reported in fish and aquatic organisms collected off the

coasts of Africa and Australia and in the Danube River in Austria (Callahan et al., 1978; Maher, 1986). Bioconcentration factors for antimony ranged from 0.15 to 390 (Callahan et al., 1978). It should be pointed out that data on the biconcentration of antimony in fish and biomagnification in higher trophic levels of animals are limited. Antimony bioconcentration was measured in voles, shrews, rabbits, and invertebrates around a smelter (Ainsworth et al., 2004). Analysis of antimony in the organs of these small mammals, compared with estimates of their antimony intake from food, showed that although the amount of antimony in the organs was elevated, it was low compared to the amount ingested. The results suggest that antimony does not biomagnify from lower to higher trophic levels in the food chain. Concentrations of these elements downstream of mining wastes were significantly higher than those in reference station sites. The pattern of accumulation of antimony in food webs decreased as follows: macroinvertebrates > bryophytes > water > fish tissues. For antimony, the lowest concentrations were found in water (Julia-Laurence et al., 2009). The relative mobility of antimony in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.8.

Table 13.8

Redox Condition	System pH	Relative Mobility of Antimony
Oxidizing	< 3	Somewhat mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Somewhat mobile
Reducing, no H_2S	> 5 to neutral	Scarcely mobile to immobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Beryllium

Beryllium is a naturally occurring element found in Earth's surface rocks at levels of <1 to15 mg/kg (Shacklette and Boerngen, 1984). The National Institute of Environmental Health Sciences reported that beryllium was detected at 2760 of 50,000 surface water sites in the United States at an average concentration of 1.9 µg/L and 30 of 334 groundwater sites at an average concentration of 1.7 µg/L (http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s022bery.pdf).

This lightest of all metals, beryllium has two common oxidation states, Be^0 and Be^{2+}. Because of its high reactivity, beryllium is not found in nature as the free metal. There are approximately 45 mineralized forms of beryllium. The important beryllium minerals are beryl and bertrandite. Beryl has been known since ancient times as the gemstones emerald (green), aquamarine (light blue), and beryl (yellow).

Most of the beryllium ore that is mined is converted into alloys and used in applications including electronics and computers, nuclear weapons, and automobiles. Because it is light, beryllium alloys are used in aircraft and pace vehicles and in sports equipment (e.g., bicycle frames, golf clubs). Medical uses include dental devices and x-ray machines.

The National Toxicology Program lists beryllium and certain beryllium compounds as human carcinogens. The primary route of human exposure to beryllium is through inhalation of dusts and fumes. Beryllium may also be ingested in drinking water or food. Low levels (10 µg/L) of beryllium in pH 4.5 waters caused gill damage in fish. Higher levels (>100 µg/L) were lethal (Jagoe et al., 1993). The relative mobility of beryllium in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the

presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.9.

Table 13.9

Redox Condition	System pH	Relative Mobility of Beryllium
Oxidizing	< 3	Somewhat mobile
Oxidizing, low iron	> 5 to neutral	Scarcely mobile to immobile
Oxidizing, high iron	> 5 to neutral	Scarcely mobile to immobile
Reducing, no H_2S	> 5 to neutral	Scarcely mobile to immobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Copper

Copper is an essential element in all plants and animals. Copper's biological role is for respiratory and red blood cell function and is present in oxidative enzymes. The U.S. Recommended Daily Intake for copper for humans varies from 200 to 1300 µg/day for infants and lactating females, respectively (http://www.iom.edu/Object.File/Master/21/372/0.pdf).

In animals, including humans, it is found widely in tissues, and concentrates in liver, muscle, and bone. It functions as a cofactor in enzymes and in copper-based pigments. Some mollusks have blue-green blood, resulting from the copper compound hemocyanin, used to transport oxygen, so their blood is blue when oxygenated rather than red as in humans, whose oxygen trasport compound is hemoglobin.

Copper may occur in Earth's crust as the free native metal or in 1+ or 2+ oxidation states, commonly with sulfide minerals as iron-containing ores such as chalcopyrite, $CuFeS_2$ (Van der Perk, 2006). Chalcopyrite is the copper mineral of the greatest economic significance (Kelly, 1988). The normal copper concentration in soils is 2 to 60 mg/kg (Bowie and Thornton, 1985).

It is important to know the speciation of copper in solution, as metal uptake by an organism often occurs in water (i.e., fresh water, seawater, and interstitial water in soils and sediments). In controlled laboratory conditions, the speciation of copper can be forecast when equilibrium is attained. In Figure 13.5 a with variables of acidity (pH) and copper concentration and a given concentration of total carbonate (10^{-3}), the resulting copper forms shown are the divalent cation, hydroxides, and carbonates. In Figure 13.5 b with variables of acidity (pH) and oxidation–reduction (Eh), the copper species formed are CuO, $Cu_2CO_3(OH)_2$, Cu_2O, Cu, and Cu_2S (Spear and Pierce, 1979).

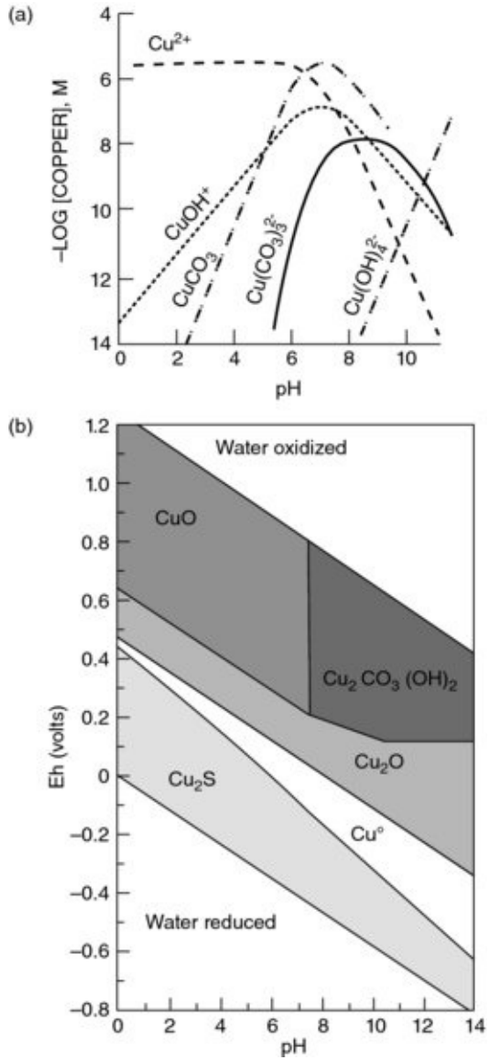


FIGURE 13.5 Copper speciation with (a) varied acidity (pH) and copper concentration, and (b) varied pH and oxidation–reduction (Eh).

The relative mobility of copper in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.10.

Table 13.10

Redox Condition	System pH	Relative Mobility of Copper
Oxidizing	< 3	Very mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Scarcely mobile to immobile
Reducing, no H_2S	> 5 to neutral	Mobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

In a mine tailings pond or in riverine or aquatic environments receiving acid drainage, the loading of different constituents may be too dynamic for equilibrium to be reached, making the prediction of metallic species present impossible except in vague terms (Ripley et al., 1996). Within a tailings pond, oxidation–reduction conditions will vary with depth, and acidity will be affected by snowmelt and precipitation,

causing metal speciation to alter seasonally. Impacts from historic metal mining, process, and smelting in the upper Clark Fork River Basin (Butte and Anaconda, Montana) have had a significant effect on aquatic resources in the river, as described in the following case study. The Clark Fork River is part of the Milltown Reservoir Superfund site, and remediation and restoration activities were begun in 2009.

Case Study: Copper, Metals, and Trout, Clark Fork River, Montana

The riverine landscape of the Clark Fork River (CFR), Montana, contains sediments contaminated with copper, cadmium, zinc, iron, arsenic, and lead that pose a significant ongoing threat to aquatic life. Copper is the worst of the contaminants, but in high enough concentrations any of these metals can cause fish mortality. Large fish kills have occurred with high flow and ice scour events. In the CFR, all aspects of a fish's environment are contaminated with metals. This includes the substrates that form the bed and banks of the river, aquatic insects that are the trout's primary food source, and the water that must pass over a fish's gills and into its system to provide it with oxygen and to carry on bodily functions.

The effects of metals contamination are manifest in trout populations in a variety of ways: in depressed numbers, in the absence of certain trout species, on growth, on the survival of young, and in reduced fecundity. Studies show that all of these contribute to the reduced fishery in the CFR. Surveys carried out by the state of Montana have found fish populations in the CFR to be about one-fifth the number in comparable area streams. Aquatic insects from the CFR contain significantly higher concentrations of metals than do insects from control streams. Studies were conducted to test insects as an exposure pathway to toxicity to evaluate whether fish with diets consisting of contaminated insects had elevated metals concentrations.

Phillips, G. R. and J. Lipton, 1995. *Injury to aquatic resources caused by metals in Montana Clark For River Basin: historic perspective and overview*. Canadian Journal of Fisheries and Aquatic Science 82:1990-1993.

Nimick, DR. 1990. *Determination of Point and Nonpoint Source Toxicity in the Clark Fork River Basin Using the Daphnid, Ceriodaphnia Dubia*. Proceedings of the 1990 Clark Fork River Symposium.

An excellent review of the hazards of copper related to fish, wildlife, and invertebrates has been published by the U.S. Fish and Wildlife Service (Eisler, 1998). For copper accumulation in aquatic animals, little or no biomagnification is evident in freshwater food chains (Stockes, 1979).

Mercury

The concentration of mercury in the Earth's crust is approximately 50 µg/kg, usually found as a sulfide mineral. Bailey and Gray (1977) reported elevated concentrations of mercury in environmental samples near abandoned mercury mines in southwestern Alaska. Soil samples near the mine contained levels approaching 1500 mg/kg, while background soils revealed much lower concentrations, 1.2 mg/kg. In general, soil levels below 100 µg/kg are considered to be within the normal range (Adriano, 2001). In aquatic environments, the methylation of mercury, which can occur in sediments and within the water column, is the pathway by which mercury enters the food chain. Methylmercury is fat soluble, which enhances the bioavailability of mercury. The demethylation and volatilization of dimethylmercury are competing processes (National Research Council, 2005). Mercury can bioaccumulate by several orders of magnitude through several trophic levels. Bald eagles, for example, tend to bioaccumulate more mercury than other organisms in the food web, as depicted in Figure 13.6. All mercury that bioaccumulates in fish tissue is methylated (Bloom, 1992; U.S. Environmental Protection Agency, 1996).

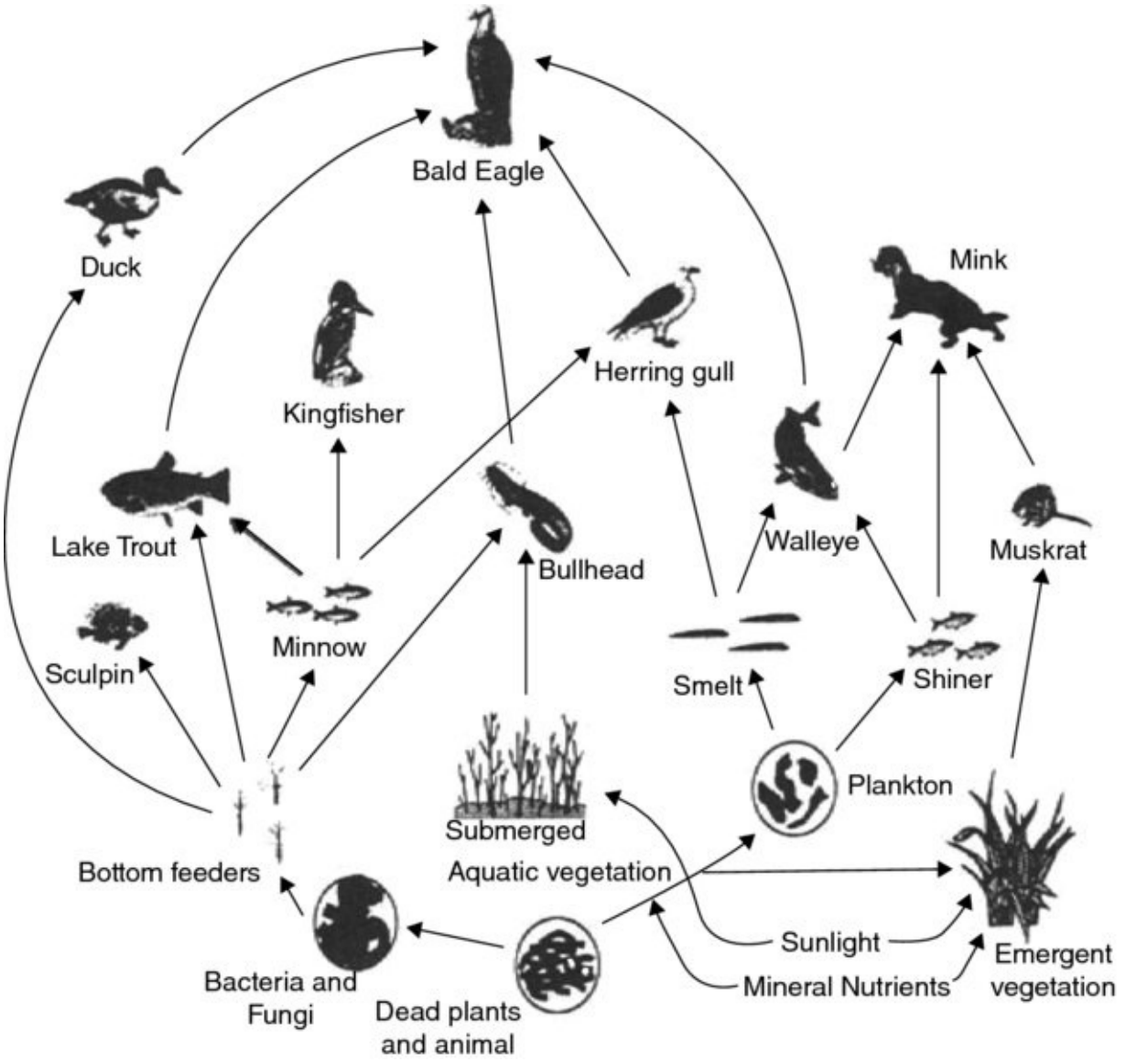


FIGURE 13.6 Conceptual aquatic food chain showing methylmercury bioaccumulation. (From U.S. Environmental Protection Agency, 1996.)

Gold mining in several rivers in the Amazon River Basin in South America has resulted in widespread contamination of several aquatic receptors, including fish. Mercury is used in mining operations to remove gold from the ore by amalgamation. Mercury is then released to the atmosphere during the heating of the alloy. Mercury concentrations in carnivorous fish from other areas contaminated by mercury show similar muscle concentrations of mercury (Lacerda et al., 1994). Several states (e.g., Montana, Alaska) have published guidelines for human fish consumption due to elevated levels of environmental contaminants, including and, in particular, mercury (http://www.dphhs.mt.gov/fish2005.pdf and http://www.epi.hss.state.ak.us/bulletins/docs/rr2007_04.pdf). Sources of mercury to the environment include both natural and anthropogenic activities. The mercury cycle is complex, but it appears that 70 to 80% of total mercury in the atmosphere is a result of human activity (Mason et al., 1994).

The relative mobility of mercury in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.11.

Table 13.11

Redox Condition	System pH	Relative Mobility of Mercury
Oxidizing	< 3	Mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Somewhat mobile
Reducing, no H_2S	> 5 to neutral	Somewhat mobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Manganese

Manganese is a transition metal with a chemistry similar to that of iron, but with three oxidation states: 2+, 3+ and 4+, or Mn(II), Mn(III), and Mn(IV). Manganese is involved in enzyme systems, helping with protein, carbohydrate, and fat metabolism, in blood clotting, and with building bone and connective tissues. The human U.S. Recommended Daily Intake for manganese is 2 mg. The standard for manganese in drinking water is 50 µg/L. Long-term exposure to manganese in industrial environments is a concern to human health, with manganese being toxic to the nervous system (http://www.atsdr.cdc.gov/tfacts 151 .html#bookmark04). Manganese is removed via aeration for drinking water. Manganese is a trace metal present in aquatic environments and can form oxide phases that can sorb other metals, natural organic material such as humic substances, and organic contaminants (McKnight and Hrncir, 2001).

Manganese is more mobile than iron and therefore more prone to leaching and transport. Under naturally occurring conditions, the formation of MnO_2 in which Mn has an oxidation state of 4+ prevails (Van der Perk, 2006). Mn oxide is precipitated preferentially on existing Mn oxide surfaces, resulting in nodule formation around a central nucleus, and coatings or discrete particles of Mn oxide are common in soils and bed sediments (Gammons et al., 2005).

The discharge of acid mine drainage is a possible anthropogenic source of manganese in stream water. Manganese usually persists in water for greater downstream distances than does iron. As the acidity is buffered and the pH increases, iron precipitates out first as ferric hydroxide, followed by manganese precipitating as black manganese oxide (Nimick et al., 2005).

In an extensive study of the processes controlling manganese chemistry in pristine and contaminated mountain streams in Colorado, McKnight and Hrncir (2001) studied the precipitation of manganese oxides and the role of humic substances in the photochemistry of iron and manganese. One common aspect of iron and Mn oxides and humic substances is their lack of chemical definition and their environmental variability. Mn(IV) is more soluble than Fe(III) at neutral pH, but the precipitation of manganese oxides can be accelerated by surfaces and microbes. Because of the relative abundance of humic substances to Fe and Mn in solution and in solid phases, interactions between humic substances and Fe and Mn play an important role in the photochemistry of these two metals. Thus, another consideration in studying Mn photochemistry is that humic substances can be photolyzed, producing reactive photoproducts such as organic radical species.

Research showed that Mn photoreduction is a process that contributes to diel variation in Mn speciation and transport in streams that have neutral pH and high Mn (Gammons et al., 2005; Nimick et al., 2005) concentrations. The extent of Mn photoreduction depends on the pH at the Mn oxide surface and on the form of the Mn oxides on the streambed. In laboratory experiments using natural Mn oxides from the stream, sorption of dissolved humic substances influenced the photoreactivity of Mn oxide surfaces. High-

pH and high-Mn concentrations are the environmental conditions that are associated with diel variation due to in-stream biogeochemical processes (McKnight and Hrncir, 2001).

August et al. (2002) looked at winter low flow and spring snowmelt shifts in a natural wetland's functions relating to drainage from an abandoned mine tunnel with high concentrations of iron, zinc, and manganese. The retention in the wetland during summer was caused primarily by precipitation of iron oxides and manganese and zinc sulfides. During autumn, winter, and spring, however, zinc and manganese mass flows to the stream were greater than mass flows from the mine adit, indicating a seasonal cycle of the wetland acting as a net sink in the summer and then a net source of Mn in the winter.

The relative mobility of manganese in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.12.

Table 13.12

Redox Condition	System pH	Relative Mobility of Manganese
Oxidizing	< 3	Very mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Somewhat mobile
Reducing, no H_2S	> 5 to neutral	Very mobile

Lead

The use of lead has a long human history. The smelting of PbS ores to recover silver and lead was developed at least 5000 years ago (Adriano, 2001). Lead is still mined and recycled in at least 50 countries (Adriano, 2001). The average Earth crust concentration was given by Swain (1978) at 13 to 16 mg/kg. The bioavailability of lead in soils for plant uptake has been estimated using several different extract solutions, from acids such as HCl to neutral salts such as ammonium acetate. In general, total lead determinations are not good indicators of its mobility or bioavailability.

Lead is a nonessential element that does not participate in any known beneficial biological functions (National Research Council, 2005). Lead affects blood, the central nervous system, reproduction, and survival. The National Academy of Sciences (1972) identified lead as the most frequent cause of accidental poisoning of animals, most emanating from dust fallout from lead smelters and mining areas. A primary lead smelter in East Helena, Montana operated for over 100 years, and cattle residing in the vicinity of the smelter were found to have significantly elevated blood lead levels compared to control animals (Neuman and Dollhopf, 1992). The blood lead concentrations were correlated with distance from the smelter and soil Pb levels. Younger cattle had higher levels than those of mature animals (Neuman and Dollhopf, 1992). Other impacts of lead from smelters on wildlife have been reported: on mammals and birds near Palmerton, Pennsylvania (Beyer et al., 1985; Storm et al., 1994) and lead poisoning of avian species near a major mining and smelting complex in northern Idaho (Henny, 2003).

Lead poisoning in fish, birds, and mammals has been summarized by Pain (1995). An excellent older literature review of lead is that of Eisler (1988).

The relative mobility of lead in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.13.

Table 13.13

Redox Condition	System pH	Relative Mobility of Lead
Oxidizing	< 3	Somewhat mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Scarcely mobile to immobile
Reducing, no H_2S	> 5 to neutral	Mobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Cadmium

Cadmium is a nonessential element that is highly toxic to humans in both dissolved and respirable forms. It acts synergistically with other toxic metals (Kabata-Pendias, 2001). Cadmium is a rare element found in association with zinc, occurring most commonly in zinc minerals (Ripley et al., 1996). The normal cadmium concentration in soils is < 1 to 2 mg/kg (Bowie and Thornton, 1985). Cadmium interferes with zinc in enzyme catalysis and key metabolic processes and in zinc bioavailability. Cadmium is bioaccumulated at all trophic levels. It is toxic to plants and animals, is readily absorbed from the environment (Jaworski, 1980), and is toxic to some plants at concentrations much lower than those of zinc, lead, and copper. Cadmium is a carcinogen and is also teratogenic (Smith, 1999). In wildlife, cadmium was accumulated in the kidneys of white-tailed deer sampled near a zinc–cadmium smelter (Sileo and Beyer, 1985); however, bioaccumulation of certain metals in wildlife is not restricted to contaminated sites. Munshower and Neuman (1979) conducted a study of metals in tissues from mule deer and antelope collected from a pristine area in southeastern Montana. Both vegetation and soil concentrations of metals were below most literature values, and copper in vegetation was described as marginally deficient.

Bioaccumulation of lead in antelope livers, and cadmium accumulation in antelope and deer kidneys as functions of animal age, were reported. The authors concluded that because of the lack of comparative data, it was not possible to ascertain whether the lead and cadmium levels in these animal tissues and the accumulations with age were normal. However, they also concluded that the general condition of wildlife populations would indicate that the elemental levels were reflective of levels in healthy deer and antelope. Other wildlife species may be much more sensitive to cadmium toxicity, as described below in the case history of cadmium poisoning in ptarmigan.

The major impact of mining on fish populations has been through acidification (Ripley et al., 1996). Most fish populations cannot reproduce below a pH of about 5 (Scheuhammer, 1991). At these low pH levels, metals, including cadmium, are readily soluble and bioavailable to aquatic receptors. An excellent older literature review of cadmium is that of Eisler (1985). Spatial and temporal scales considered for wildlife need to be different than those used to evaluate metal exposure to invertebrate and plant communities. Sophisticated wildlife exposure models will take into account foraging behavior of individual animals in the population, the food and habitat quality, and the spatial distribution of habitat and contamination.

Case History: Cadmium and Ptarmigan, Leadville, Colorado

Brittle bone disease in a population of Rocky Mountain white-tailed ptarmigan (*Lagopus leucurus)* in Colorado was a result of trophic transfer of cadmium in soil and/or stream water to the bark of willows, then to the birds. The ptarmigans' bone calcium was decreased. The study determined how ecological

variability could influence exposure by characterizing the birds' diet preferences in time and space (i.e., seasonal foraging ranges); it linked reproductive effects and population survival observed to metal accumulations in target organs, toxicity threshold, and toxicological indicators. Results indicate that cadmium toxicity may often go undetected or unrecognized and that cadmium toxicity may be more common among natural populations of vertebrates than previously recognized. The research shows that ingestion of even trace quantities of cadmium can influence the physiology and health of individual organisms, and the demographics and distribution of species (Larison et al., 2000).

Hope, B. 2001. *A case study comparing point estimate and spatially explicit ecological exposure analysis methods*. Risk Analysis 21(6): 1001-10.

The relative mobility of cadmium in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.14.

Table 13.14

Redox Condition	System pH	Relative Mobility of Cadmium
Oxidizing	< 3	Very mobile
Oxidizing, low iron	> 5 to neutral	Very mobile
Oxidizing, high iron	> 5 to neutral	Mobile
Reducing, no H_2S	> 5 to neutral	Mobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Chromium

Chromium is a hard steel-gray metal resistant to oxidation. It exists in several oxidation states, including Cr^{3+}, which is essential for normal metabolism of insulin and glucose in humans (Langard and Norseth, 1979) and for regulating carbohydrate metabolism in mammals (Preston et al., 1976). Chromium in the 6+ oxidation state is toxic and a carcinogen. Chromium in the 6+ state is produced in industrial processes, and soils and waters in close proximity to these facilities can have elevated concentrations. Typical soil levels range from 5 to 1000 mg/kg with a mean about 49 mg/kg (Kabata-Pendias, 2001). Freshwater concentrations vary from 0.18 to 1 µg/L (Pais and Jones, 1997).

The solubility of chromium is significantly affected by solution pH, with the least solubility between pH 5.5 and 8.0 (Pais and Jones, 1997). Studies of acute toxicities of Cr^{6+} and Cr^{3+} to aquatic organisms show the Cr^{6+} form to be more toxic and sensitivity is correlated with life stage (Eisler, 1986). No biomagnification of Cr has been observed in food chains, and concentrations are usually highest at the lowest trophic levels (Eisler, 1986).

The relative mobility of chromium in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.15.

Table 13.15

Redox Condition	System pH	Relative Mobility of Chromium
Oxidizing	< 3	Somewhat mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Scarcely mobile to immobile
Reducing, no H_2S	> 5 to neutral	Somewhat mobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Silver

Silver is a soft, malleable metal with a characteristic sheen. It is most often found in nature as the mineral argentite (Ag_2S). Soil concentrations vary from about 0.03 to 0.9 mg/kg, and fresh water may contain 0.13 µg/L (Pais and Jones, 1997). Common valence states are Ag^0, Ag^+, and Ag^{2+}. The hydrated or “free” silver species is very toxic to aquatic organisms at low concentrations. The acute concentration for aquatic life (EPA Ambient Water Quality Criteria) is 1.6 µg/L. Silver is a nonessential element and has no known biological purpose. Silver as ionic Ag^+ is one of the most toxic metals known to affect aquatic organisms in laboratory testing, although large industrial losses to the aquatic environment are probably infrequent because of its economic value as a recoverable resource (National Association of Photographic Manufacturers, 1974; Nebeker et al., 1983). Silver is of concern in various aquatic ecosystems however, because of the severity of silver contamination in the water column, sediments, and biota (Luoma and Phillips, 1988). An excellent older review of silver hazards to fish, wildlife, and invertebrates is that of Eisler (1996). More current research focuses on changes in gill membrane uptake of low levels of silver (Bury, 2005), thiosulfate and dissolved organic matter protection from silver (Rose-Janes and the Playle, 2000), and the bioavailability of silver species (Wood et al., 2004).

The relative mobility of silver in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.16.

Table 13.16

Redox Condition	System pH	Relative Mobility of Silver
Oxidizing	< 3	Somewhat mobile
Oxidizing, low iron	> 5 to neutral	Scarcely mobile to immobile
Oxidizing, high iron	> 5 to neutral	Scarcely mobile to immobile
Reducing, no H_2S	> 5 to neutral	Scarcely mobile to immobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Thallium

Thallium is a soft silvery gray metal found in trace amounts in Earth's crust. Soil concentrations vary from 0.2 to 2.8 mg/kg, with a mean of 0.2 mg/kg (Pais and Jones, 1997). The level of this element in fresh water is near 0.03 µg/L. It is used mostly in the manufacture of electronic devices, semiconductors, and in some cardiac medical tests. Thallium is not essential for plants or animals and enters the environment

during the burning of coal and the manufacture of cement. According to the ATSDR, thallium is not known to be carcinogenic, to cause birth defects in humans, or to affect reproduction. However, inhalation may cause adverse health effects. The Occupational Safety and Health Administration has set an exposure limit of 0.1 mg/m^3 for thallium in workplace air. The National Institute for Occupational Safety and Health has recommended that 15 mg/m^3 of thallium be considered immediately dangerous to life and health.

Thallium is reported to be highly toxic to aquatic organisms, but data to support this statement are scarce, due primarily to thallium's low concentration in environmental media and relatively poor detection limits by conventional quantification instruments (Cheam, 2001). Early studies (Wallwork-Barber et al., 1985) examined the transport of thallium in water, sand, vegetation, and fish. They reported thallium levels increased by a factor of 10 in vegetation and fish. The EPA has yet to establish acute or chronic concentrations for fresh-or saltwater organisms.

The relative mobility of thallium in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.17.

Table 13.17

Redox Condition	System pH	Relative Mobility of Thallium
Oxidizing	< 3	Somewhat mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Somewhat mobile
Reducing, no H_2S	> 5 to neutral	Somewhat mobile
Reducing, H_2S	> 5 to neutral	Somewhat mobile

Nickel

Nickel is a silvery hard metal that takes a high polish. It occurs most often in minerals with sulfur and iron and with arsenic. It is ubiquitous in the environment with an Earth crust concentration of about 80 mg/kg (Adriano, 2001). In soils of the United States, the nickel content ranges from less than 5 to about 700 mg/kg (Shacklette et al., 1971). In unsaturated soils, this element may be found on exchange sites, bound with organic matter and microorganisms, or tightly bound in a clay lattice, and in other chemical forms (Adriano, 2001). In saturated soils, nickel is in the free form (Ni^{2+}) or complexed with organic and inorganic ligands. Like many other metals, nickel bioavailability from soils depends on total nickel content, pH, cation-exchange capacity, texture, and organic matter content.

Nickel is an essential element for plants and is involved in several enzyme reactions, urease, methyl coenzyme M reductase, hydrogenase, and CO_2-dehydrogenase (Hausinger, 1992). Deficiency of nickel in plants is well established for several species, and at elevated levels, nickel is phytotoxic to plants. Mance (1987) provided a review of the toxicity of nickel to freshwater fish and invertebrates. In general, Ni^{2+} is relatively nontoxic to fish and effects are mitigated by hardness (Adriano, 2001). However, chronic exposure to low levels of nickel affects calcium metabolism and diffusion capacity of the gill (Moore, 1991). Histopathological changes in the gill, liver, kidney, and intestine of freshwater fish exposed to sublethal levels of nickel chloride were noted (Athikesavan et al., 2006).

The relative mobility of nickel in surficial environments (Smith and Huyck, 1999) under various

conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.18.

Table 13.18

Redox Condition	System pH	Relative Mobility of Nickel
Oxidizing	< 3	Very mobile
Oxidizing, low iron	> 5 to neutral	Somewhat mobile
Oxidizing, high iron	> 5 to neutral	Somewhat mobile
Reducing, no H_2S	> 5 to neutral	Mobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Selenium

Selenium is classified as a metalloid. It is chemically similar to sulfur in its form and compounds and therefore has many interactions in plants and animals (Adriano, 2001). This element has several oxidation states, and in soils the main ions are selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}). Selenium concentrations in U.S. soils vary considerably: from trace amounts to 82 mg/kg. Seleniferous soils in the United States are known from North Dakota to Texas.

Selenium is an essential element for animals and perhaps some plant species known to be selenium accumulators (Adriano, 2001). Both deficiencies and toxicities in livestock have been reported worldwide. Excessive amounts of soil selenium are expected in arid and semiarid regions in soils derived from Cretaceous shales (Rosenfeld and Beath, 1964). The chemical form of selenium determines its mobility and bioavailability to plants and animals. Adverse effects of selenium in wild aquatic birds have been documented as a consequence of pollution of the aquatic environment by subsurface agricultural drainwater and other sources (Hoffman, 2002). In the 1980s, many birds were killed at the Kesterson Reservoir and National Wildlife Refuge (Ohlendorf, 2002), and this event has resulted in a large number of investigations and a body of literature dealing with the biogeochemistry of selenium (Weres et al., 1989; Adriano, 2001; Van Kirk and Hill, 2006).

Oxidation–reduction of selenium, methylation–demethylation, and volatilization of selenium are major areas of study in soil an aquatic environments (Adriano, 2001). Interactions between selenite and selenate in soils and waters and their relative mobility and bioavailability have been investigated. More recently, phosphate mining operations in southeastern Idaho have exposed selenium that was originally sequestered in the subsurface. Sheep grazing in these areas have died as a result of high Se concentrations in forage and water (Fessler et al., 2003). The Agency for Toxic Substances and Disease Registry (2003) recommended that children under the age of 7 should not eat more than four 4-oz meals per month of yellowstone cutthroat and brook trout from the East Mill Creek in southeastern Idaho because of elevated selenium in the fish tissue. Dietary selenium (sodium selenite) is more than 600 times more toxic than background levels of selenium in water. It has an affinity to ovaries and at high levels concentrates in the liver (Hodson, 1988).

The relative mobility of selenium in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.19.

Table 13.19

Redox Condition	System pH	Relative Mobility of Selenium
Oxidizing	< 3	Mobile
Oxidizing, low iron	> 5 to neutral	Mobile
Oxidizing, high iron	> 5 to neutral	Somewhat mobile
Reducing, no H_2S	> 5 to neutral	Scarcely mobile to immobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Zinc

Zinc is a blue-white soft metal and ranks fourth among metals in annual production: behind aluminum, copper, and iron. The most important mineral for commercial use is zinc sulfide (Adriano, 2001). The concentration in the Earth's crust is about 70 mg/kg (Krauskopf, 1979). In soils, zinc levels vary from about 10 to 300 mg/kg (Swaine, 1955), although concentrations of 900 mg/kg are found, and a reasonable mean value of 50 to 90 mg/kg was reported by Adriano (2001). Water-soluble zinc and zinc on colloidal exchange sites are considered to be bioavailable. Factors affecting zinc movement in the terrestrial environment are pH, oxidation–reduction potential, the amount of organic matter, cation-exchange capacity, and various forms of the metal.

Zinc is an essential element for plants and is involved in several metalloenzymes, including protein synthesis and transformation of carbohydrates (Kochian, 1993). Zinc deficiencies are common in plants grown in calcareous soils, due to inhibited Zn bioavailability in alkaline pH conditions. Elevated concentrations of zinc as a result of human activities can result in phytotoxic conditions. Examples include soils near a zinc smelter in Sudbury, Ontario and near Palmerton, Pennsylvania (Beyer and Storm, 1995).

Zinc is an essential element in animal nutrition. More than 200 zinc enzymes and proteins have been identified (Hambidge et al., 1986). Deficiencies of zinc are related to inadequate intake, and zinc toxicity in humans is usually related to accidental intake. For aquatic organisms, zinc is both an essential element and in some instances an environmental contaminant. Fish intestine is potentially the most important route of zinc absorption, yet little is known regarding this uptake pathway for zinc in fish (Glover and Hogstrand, 2003).

The relative mobility of zinc in surficial environments (Smith and Huyck, 1999) under various conditions of redox, the presence or absence of abundant iron and sulfur (H_2S), and pH is shown in Table 13.20.

Table 13.20

Redox Condition	System pH	Relative Mobility of Zinc
Oxidizing	< 3	Very mobile
Oxidizing, low iron	> 5 to neutral	Very mobile
Oxidizing, high iron	> 5 to neutral	Mobile
Reducing, no H_2S	> 5 to neutral	Mobile
Reducing, H_2S	> 5 to neutral	Scarcely mobile to immobile

Trace Metal Assimilation by Aquatic Organisms

Aquatic organisms assimilate metals from the dissolved content of the surrounding water and from metals contained in diet items. The results of this assimilation can affect all levels of biological organization (Peplow and Edmonds, 2005). Here we first cover aspects of trace metals that are common among aquatic organisms, including the uptake of diet-borne and dissolved metals, the regulation of metals within organisms, and variability in metal concentration. Aspects of metal incorporation and toxicity that are unique to each trophic level are discussed. Finally, community-level effects and useful tools for predicting toxic effects are explored.

Assimilation of Dissolved Metals

Three factors affect dissolved metal assimilation: the characteristics of a metal solution, dissolved metal concentration, and biotic characteristics. Within a solution, metals compete with other metals, with protons (H^+), and with dissolved organic carbon for binding sites on an organism (Vijver et al., 2004). Dissolved metal concentration is the primary factor controlling uptake in aquatic organisms. Positive diffusion gradients from the water to the organism are common in aquatic organisms because the concentration of metals is usually higher in the environment than in an organism (Langston and Spence, 1995). Biotic characteristics that affect incorporation of dissolved metals include exposure history, permeability of tissues, surface area available for absorption, and the quantity and availability of exchange sites (Langston and Spence, 1995). Variations in all three of these factors cause variation in metal assimilation rates among trophic groups, species within trophic groups, and even individuals within a species (Langston and Spence, 1995; Wang and Fisher, 1999a,b; Rainbow, 2002). Biofilms, invertebrates, and fish can all assimilate dissolved metals.

Assimilation of Metals in the Diet

Absorption of metals from the diet is a function of the concentration of metals in the diet, the volume of diet, and the processing rate of diet items (Schlekat et al., 2005). Because mechanisms for processing food and preferred diet items vary dramatically among species, the following generalizations regarding the effect of gut processes on metal uptake come with caveats (as discussed by Campbell et al., 2005). Metals associated with cell membranes and cell walls are not digested, whereas metals in the cytoplasm are readily assimilated (Campbell et al., 2005). The selection of diet items will vary the amount of metals in the diet, while an increased processing rate will reduce an organism's contact time with contaminated diet items. Absorption of trace metals from the diet is limited to invertebrates, fish, and wildlife that consume aquatic prey.

Regulation of Metals Within Aquatic Organisms

The internal concentration of excess essential metals (i.e., copper and zinc) and all other trace metals can be modestly regulated. Metals such as zinc and copper are essential for metabolism at certain levels. However, cadmium, lead, and mercury have no essential level in any organism and are toxic at all levels. Excess copper and zinc and all other trace metals are sequestered to be metabolically inactive as rapidly as possible [see Evans et al. (2006) for estimates of elimination rates]. Sequestration of metals has two major advantages: The levels of essential metals can be maintained while surplus amounts can be sequestered. However, all nonessential metals are sequestered (Vijver et al., 2004). Evolutionarily, the ability to sequester metals is advantageous in environments where trace metal concentrations fluctuate or are found only in very low concentrations. Organisms can remove the necessary metals when they are

available and sequester toxic levels of metals when they are too high. When dissolved metal concentrations become high, the sequestration ability of fish is critical in avoiding toxic effects. A balance between the rate of uptake and the rate of sequestration allows organisms to maintain biological activity.

Unsequestered metals are toxic, but once sequestered, trace metals are biologically inactive to an organism. However, the capacity to sequester metals is limited, and often the assimilation rate outpaces the capacity to sequester (Figure 13.7). This imbalance results in a buildup of unsequestered metals in an organism. When the buildup of unsequestered metal reaches a critical threshold, an organism experiences toxic effects (Figure 13.7). Invertebrates and vertebrates sequester metals in a similar manner. Trace metals are first bound to metallothionein proteins (Roesijadi, 1992; Cain et al., 2006). Metallothioneins are soluble proteins present in all organisms. They have a high binding capacity for metals, and their production increases during metal exposure (Hodson, 1988). Metallothioneins with bound metals are then sequestered to the cytoplasm and eventually are converted to insoluble intercellular granules (Hopkin, 1989; reviewed by Rainbow, 2007). Metals are added to these granules, which either remain in the organism or are shed, depending on their location within the organism. For example, metallothionein production in yellow perch (*Perca flavescens)* and the floater mollusk (*Pyganodon grandis)* increased linearly with metal exposure, and the metal content of granules increased as metal uptake increased (Campbell et al., 2005). Once bound in these granules, metals are considered sequestered and biologically unavailable within an organism. Further, metals associated with these granules are less available to a predator if the organism is consumed.

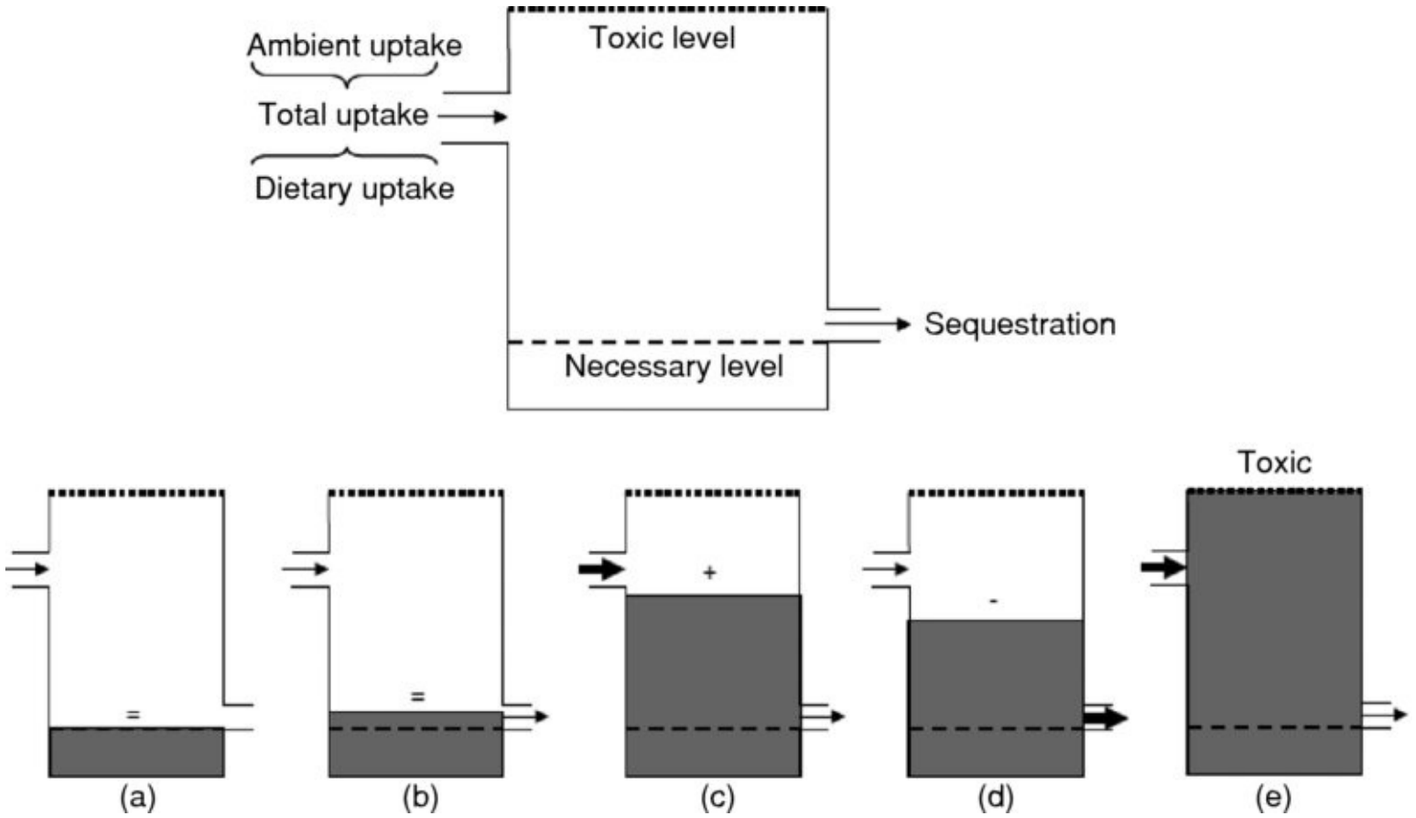


FIGURE 13.7 Schematic diagram of metal uptake, with several scenarios. The shaded area represents the level of total metal in an organism. The long-dashed line represents the level necessary for biological function; the short-dashed line represents a toxic level. The arrow size represents the relative rate of movement. Scenario: (a) No anthropogenic metals present; organism is maintaining appropriate levels of metals. (b) Anthropogenic metals present but sequestered adequately. (c) Anthropogenic metals uptake outpacing sequestration; total level approaching toxic levels. (d) Metal levels high but sequestration is outpacing uptake, indicating a history of higher exposure. (e) Uptake outpaces sequestration, causing metals to be toxic.

Trace Metal Assimilation by Primary Producers

Metals are readily taken up by aquatic plants, riparian plants, plankton, and biofilm (Holding et al., 2003). Biofilm is the base of aquatic food webs and includes bacteria, algae, diatoms, and fungi growing in a polysaccharide matrix. In unpolluted environments, copper levels of aquatic plants range from 1 to 19.3 mg/kg dry weight. Polluted environment levels can range from 120 to 1450 mg/kg dry weight (Fernandes and Henriques, 1991). Plankton are particularly important in the transfer of methylmercury to higher trophic levels (Stewart et al., 2008). Mercury is converted to the highly bioavailable form methylmercury in anoxic sediments of lakes (Boudou et al., 2005) and is transported by plankton from the sediments to the surface of a lake (or wetland) and into the food web (Stewart et al., 2008).

Accumulation of metals by rooted riparian and aquatic plants can be from two sources; sediments or the surrounding aquatic media. Incorporation of metals in biofilm is enhanced, compared to rooted plants, because of the availability of metals in the surrounding aqueous solution (Fernandes and Henriques, 1991; Hill et al., 2000). Further, biofilms in flowing waters have higher metal concentrations than those of the same composition biofilms in standing water (Hill et al., 2000). Metal absorption is enhanced in flowing waters because water is continually moving past biofilms, replenishing the source of trace metals. Metal uptake may also be enhanced by biofilms because they tend to collect colloidal metal deposits (Newman

and McIntosh, 1989; Farag et al., 2007). Trace metals are taken up and released dynamically by biofilms (Figure 13.8). Concentrations of copper, zinc, and cadmium have been shown to fluctuate hourly with changes in the surrounding concentration (Wong et al., 1984; Hill et al., 2000; Meylan et al., 2003). Metal concentrations in biofilms may fluctuate at factors 2 to 1000 times higher than the concentrations of the surrounding water (Wong et al., 1984).

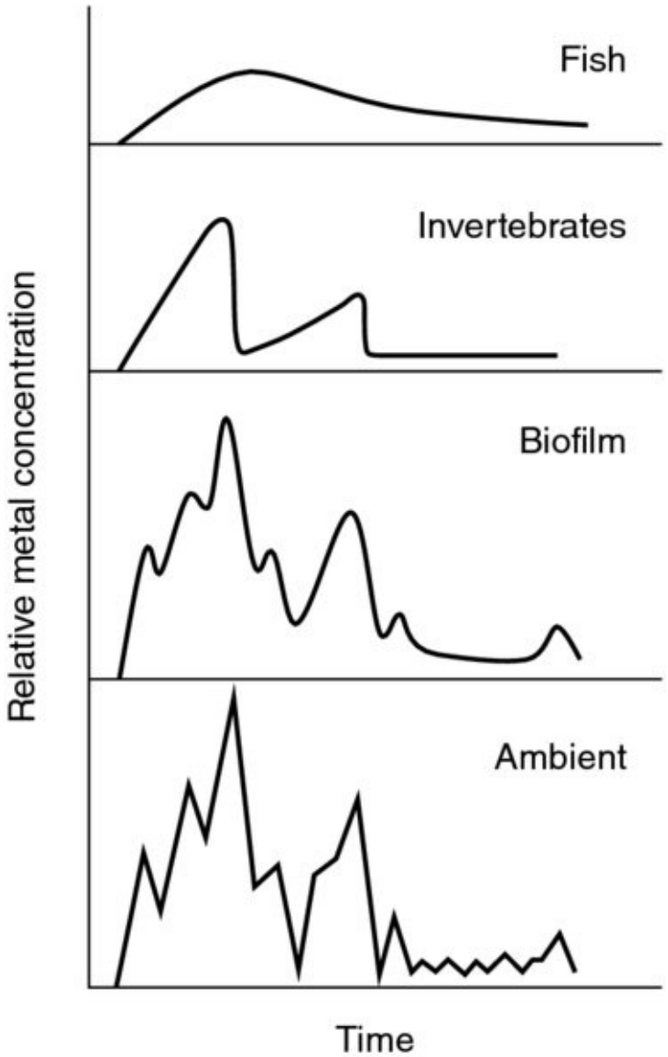


FIGURE 13.8 Relative concentration of total metal in an organism after exposure to the same history of ambient concentration. *Note:* There are vertical drops in invertebrate concentration because metals can be shed during molting.

Toxic Effects of Trace Metals to Primary Producers

Trace metals affect biofilm communities over the short term (i.e., hours) by reducing photosynthetic rates and over the long term (i.e., days) by shifting species composition and abundance (Serra et al., 2009). Even if trace metals do not have direct toxic effects on biofilms, incorporation at this level is an important step in transferring the metals to higher trophic levels. For example, little is known about the toxicity of mercury to biofilms, but biofilms can accumulate mercury to concentrations thousands of times higher than that of the surrounding water. The organic and inorganic forms of mercury (methylmercury and Hg^{2+}, respectively) are then easily transferred by grazing invertebrates to higher trophic levels (Hill et al., 1996).

As suggested previously, metal absorption and toxicity are closely related to photosynthesis. Light has

been shown to mediate the assimilation and effects of copper (Fernandes and Henriques, 1991), cadmium (Pawlik and Skowroński, 1994; Hill et al., 2000), and zinc (Nimick et al., 2005). In a wide variety of experiments on several trace metals, photosynthesis was reduced, sometimes to senescent levels, after several hours of exposure to trace metals (Hill et al., 2000). Copper is an essential metal for growth (Sandmann and Böger, 1980; 1983; Sunda, 1989), but it is particularly toxic to plants in polluted environments (Fernandes and Henriques, 1991). Copper affects electron transport and chloroplast function (reviewed by Fernandes and Henriques, 1991) and causes deformities in algae (Guasch et al., 2002). Copper also shifts community structure in biofilms (Guasch et al., 2002; Massieux et al., 2004), and these changes can happen in as few as 3 days (Boivin et al., 2005). Cadmium affects photosynthesis (Hill et al., 2000) but has also been shown to reduce diatom growth, shift species abundance, and cause deformities (Morin et al., 2008). After chronic exposure to copper (12 weeks), biofilms shifted from a community once dominated by Cyanophyceae to a community dominated by Chlorophyta. No difference in photosynthesis rates was observed when copper concentrations were 1 µM or less. However, photosynthesis was reduced at concentrations of 5 µM copper or higher (Soldo and Behra, 2000; Massieux et al., 2004). Chronic exposure to copper also increased the community's tolerance to zinc, nickel, and silver. This tolerance to additional metals is likely because the dominant taxa in the copper-exposed treatments were also tolerant to these other metals (Soldo and Behra, 2000). The shift to a metal-tolerant community can take as few as several days. However, recovery of diversity and composition can take longer than 28 days, even if the community is inoculated with the original species (Boivin et al., 2006).

In summary, trace metals taken up by biofilms can reduce photosynthesis rates after hours of exposure. Within days of exposure, metals can reduce community-wide photosynthesis and cause deformities. After chronic exposure, community-wide photosynthesis often returns to preexposure levels; however, photosynthesis is carried out by a community composed of metal-tolerant species. While the metal-tolerant community may perform the same functions (e.g., photosynthesis) as a reference community, no shift back to the reference condition has been documented.

Trace Metal Assimilation by Aquatic Invertebrates

Invertebrates are an important link between accumulation of trace metals in plants and higher trophic levels (Stewart et al., 1993). Aquatic invertebrates readily accumulate trace metals, but the concentration of accumulated metals can vary greatly among species in the same genus (Rainbow, 2002) or even among species in the same feeding guild (Goodyear and McNeill, 1999). For example, in a single species of caddis fly (*Hydropsyche californica*), the total body concentrations of cadmium, copper, lead, and zinc were higher in contaminated sites than in reference sites (Cain et al., 2000).

Invertebrates assimilate trace metals through a permeable outer surfaces or through the gut (Hare, 1992). The exoskeleton is often considered a barrier to metal incorporation, helping invertebrates to control the absorption rates of metals (Mason and Jenkins, 1995). However, trace metals can be passively absorbed into the exoskeleton, contributing to total metal concentration. This source is small and does not become incorporated physiologically (Rainbow, 2002). Most uptake is through other permeable surfaces (e.g., gills) from the surrounding water or through the gut from the diet (Meyer et al., 2005; Rainbow, 2007).

All metals, after being taken into organisms, are metabolically active; essential metals are used for metabolic processes, and nonessential metals are sequestered. Essential metals are actively incorporated into the cytosol (cellular fluid), while nonessential metals move passively into cells. Once in the cytosol the metals can interact, beneficially or harmfully, with cellular processes. In an example invertebrate, 30 enzymes require 26.3 µg/g dry weight copper and 80 enzymes require 34.5 µg/g dry weight zinc

(Rainbow, 2007). Measurement of cytostolic metals is the most appropriate gauge of metals in invertebrates because these metals are the most biologically active and the most easily transferred to fish (Cain et al., 2000).

Sequestration sites are closely linked to uptake sites (Vijver et al., 2004). Assimilation of ambient metal through permeable outer surfaces results in a distribution skewed toward surface deposits (e.g., chiton, exoskeleton). Uptake from the diet results in metals being deposited in tissues of the digestive tract (Campbell et al., 2005). It should be noted that molting can involuntarily reduce the total metal concentration in invertebrates, an advantage that invertebrates share over other groups of aquatic organisms (Campbell et al., 2005). Molting would cause rapid decreases in total metal concentration (Figure 13.8). However, this only reduces the sequestered component of total metals and leaves the unsequestered (i.e., biologically available) metal concentration unchanged. Although invertebrates can use these processes for modest control of trace metal levels, all metals will be toxic if the rate of sequestration cannot keep pace with the rate of uptake (see Figure 13.7).

Toxic Effects of Metals to Invertebrates

Trace metals reduce the function of organs by reducing metabolic processes and growth. Invertebrates commonly exhibit reduced energy metabolism and increased energy expenditure as a response to stress caused by trace metal toxicity (Maltby, 1999). For example, chironomid larvae grew less in cadmium-contaminated sediments than in uncontaminated sediments (Wentsel et al., 1977). Toxic concentrations and metabolic effects vary widely among species and metals (Rainbow, 2002; Buchwalter et al., 2007). For example, the zinc concentration of one species of mayfly at an uncontaminated sites may be the toxic level for another species at the same site. Despite the differences among taxa, caddis flies of the genus *Hydropsyche* and mayflies of the genus *Baetis* are generally considered tolerant of trace metal pollution. However, most other mayflies are considered intolerant of metal pollution (Clements, 1994; Clements and Kiffney, 1995; Cain et al., 2000, 2004).

Trace metal toxicity has been demonstrated in a wide variety of species and environmental circumstances (Hare, 1992). Chronic exposure lowers the concentration necessary for a toxic effect. For example, toxic concentrations were 11 times lower in a 28-day exposure than a 7-day exposure for cadmium-exposed mayflies (Spehar et al., 1978). Shifts in community structure start with the least tolerant taxa and progress toward the most tolerant taxa (Cain et al., 2004). The total number of taxa, number of EPT taxa [mayfly (*Ephemeroptera*), stonefly (*Plecoptera*), and caddis fly (*Trichoptera*)], abundance of the four major feeding groups (scrapers, shredders, collectors, and predators), and abundance of metal-sensitive taxa are commonly used to measure the effects of metals on invertebrate assemblages (Clements and Kiffney, 1995; Carlisle and Clements, 1999). Decreases in these metrics have been well documented in mining-affected waters (e.g., Clements, 1994; Clements and Kiffney, 1995; Beltman et al., 1999; Clements et al., 2000; Giddings et al., 2001; Maret et al., 2003). While this pattern indicates that there are differences between mining and reference sites, it does not identify the cause of the variation. The differences could be caused by a multitude of physical, chemical, or ecological factors (Clements, 2004). The physiology of metal toxicity is not well understood for invertebrates. Metals can be directly toxic but can also have sublethal and other indirect effects (Fisher and Hook, 2002). Therefore, shifts in invertebrate abundance or species composition may be attributed to shifts in habitat structure or food availability rather than being directly attributed to toxic metals (e.g., Cain et al., 2004).

Elevated concentrations of trace metals in macroinvertebrates signal a likely cause of impairment. However, it is difficult to separate the effect of metals from differences in site characteristics or the effect of other ecological shifts (Clements and Kiffney, 1995). It is important to make this distinction because

critics of biomonitoring can reasonably explain differences in species abundance or composition as being caused by differences between sites in physical, chemical, or ecological variables. However, small-scale experiments that manipulate metal concentrations and control for confounding physical, chemical, or ecological factors have begun to demonstrate a causal relationship between elevated metal concentration and changes in species abundance or composition (Clements, 2004).

In summary, trace metals are readily taken up by aquatic macroinvertebrates, and this group is an important link between metals accumulated by primary producers and those accumulated at higher trophic levels. Caddis flies of the genus *Hydropsyche* and mayflies of the genus *Baetis* are more tolerant of metals than are other invertebrates. Their presence, along with the total number of taxa, number of EPT taxa, and abundance of the four major feeding groups are commonly used as indicators of metal exposure and the response of aquatic communities.

Trace Metal Assimilation by Fish

Fish are unique among vertebrates in that they can assimilate metals from their diet and from the surrounding environment through their gills and skin (Bury et al., 2003). Uptake across the skin is generally considered negligible, with the main pathways of trace metal absorption being across the gills and through the digestive tract (Dallinger et al., 1987; Bury et al., 2003). Assimilation of metals via these two routes is the same (Clearwater et al., 2002). Acute exposure leads to accumulation of metals in the gills, while chronic exposure leads to accumulation in the gut. The difference in accumulation sites may be metal-specific. For example, zinc tended to accumulate in the carcass (89 to 90%) rather than in the gills (4 to 6%; Sappal et al., 2009). Different diet items may also lead to differences in metal exposure. For example, Farag et al. (1999) fed metal-contaminated invertebrates from two polluted rivers to cutthroat trout (*Oncorhynchus clarki lewisi*). For unexplained reasons the less contaminated invertebrates caused a higher metal concentration in fish, suggesting that the metals were somehow more bioavailable (Farag et al., 1999).

Fish can regulate metal exposure through changes in behavior and internally using metallothionein proteins; however, these processes only gradually change internal metal concentration (Figure 13.8). Fish are unique in that they can detect and avoid metal-contaminated water, thus limiting exposure to trace metals. This behavior was demonstrated in similar experiments using rainbow trout (*Oncorhynchus mykiss*), brown trout (*Salmo trutta*), and cutthroat trout (Woodward et al., 1997; Hansen et al., 1999a,b).

Cutthroat trout and rainbow trout detected and avoided zinc concentrations as low as 28 µg/L. Even after a 90-day acclimation to 55 µg/L zinc, cutthroat trout were able to detect, and preferred, lower concentrations (Woodward et al., 1997). Rainbow trout avoided a mixture of metals meant to simulate a contaminated river (Hansen et al., 1999). Brown trout were less sensitive to metal-contaminated water, possibly explaining why brown trout populations seem to be less severely affected in metal-contaminated rivers (Hansen et al., 1999a,b). Bull trout (*Salvelinus confluentus)* were not affected dramatically by waterborne copper. Bull trout accumulated higher copper concentrations than those associated with reduced growth in rainbow trout. This species may be less sensitive to metal-contaminated water because of their slower growth rate (Hansen et al., 2002). Metal avoidance would be an advantage only during acute exposure, where fish can temporarily congregate in water with a lower metal concentration (e.g., tributaries or groundwater inflow). Under chronic metal contamination, this behavior would cause limitations in food and habitat and could, in part, be responsible for reduced populations (Woodward et al., 1997).

Fish can also regulate internal metal concentrations using metallothionein proteins. For example, excess metals from the diet can be trapped by metallothionein proteins in cells of the gut lining (Olson et al.,

1978). These cells are then potentially sloughed and excreted as feces, along with mucus (Bury et al., 2003). Both the gills and the gut can transfer metals into the bloodstream, where they are rapidly transferred to other organs (Campbell et al., 2005). For example, in caged rainbow trout, cadimum accumulated in the spleen and muscle; mercury in the muscle and kidney; lead in the bone, spleen, and muscle; chromium in the spleen, muscle, and gills; and copper in the kidney (Camusso et al., 1995). Further, these tissue levels were higher in metal-contaminated sites than in uncontaminated sites (Camusso et al., 1995). Dietary copper accumulates in the intestine, liver, and gallbladder and, to a lesser degree, in the gill, muscle, and kidney. Zinc accumulates in the stomach, kidney, liver, and gills and, to a lesser degree, in the gonads, spleen, and skin (reviewed by Clearwater et al., 2002). Transfer to other organs can be within 1 to 12 hours for zinc (Wekell et al., 1983, 1986) and 24 to 72 hours for copper (Clearwater et al., 2000).

Toxic Effects of Trace Metals to Fish

Metals can have sublethal effects, affect species presence and abundance, and be directly toxic to fish. Trace metals can be important for several metabolic functions of fish, including cellular respiration and enzyme activity. However, in excess they can form free radicals, bind to the inappropriate metabolic pathways, interrupt the normal function of calcium and magnesium, and alter DNA transcription (Bury et al., 2003; Finn, 2007). Metal binding to sulfhydryl groups on proteins is particularly disruptive to metabolic processes (Hodson, 1988). Zinc caused inhibition of protein synthesis in gill cells when fish were exposed to zinc in the water (Sappal et al., 2009). Early life stages of fish can take up a wide variety of trace metals, including cadmium, chromium, copper, lead, manganese mercury, molybdenum, silver, and zinc (Finn, 2007). However, eggs are resistant to metal incorporation during fertilization and after deposition because of the protective chorion, or outer membrane, of the embryo (Farag et al., 2006a,b). Juvenile fish may be more prone to metal accumulation because they are feeding on potentially contaminated invertebrates (Maret and MacCoy, 2002).

Sublethal effects of trace metals in fish include loss of equilibrium, reduced energy stores, decreased feeding rate, changes in social hierarchy, anemia, decreased diet assimilation efficiency, constipation, decreased growth, organ lesions, and DNA alteration are discussed in the literature (Handy, 2003; Handy et al., 2003). Metal exposure causes vacuoles to form in the brain, degeneration of the pyloric caeca, and hypertrophy and hyperplasia of the gills (Farag et al., 1999). These effects reduce feeding activity, growth, and reproduction rate and can eventually depress or extirpate populations (Woodward et al., 1997; Farag et al., 1999). Sublethal effects, such as avoidance of metal-enriched waters, may not be toxic to fish but can explain gradual loss of species or reduced abundance in affected waters.

The presence and abundance of fish can be affected by lower growth rates, lower fecundity, and avoidance of metal-contaminated water. For example, lower abundance and fewer native species were present in mining-affected rivers in Idaho (Maret and MacCoy, 2002). Of 18 species collected, sculpins (Cottidae) were particularly affected, and they were more severely affected than were salmonids (Maret and MacCoy, 2002).

Metals can be directly toxic to fish when present in their diet, the water, or combinations of these sources (Wekell et al., 1983; Lanno et al., 1985; Farag et al., 1999). When survival is used as an endpoint, metal toxicity can range from 7 to 100%, depending on metal concentration and exposure duration. The mode of uptake can also play a role in survival. For example, dietary exposure of fish was most toxic when naturally incorporated into invertebrates (Woodward et al., 1997; Farag et al., 1999). Exposure to metal-contaminated water also reduced survival of Chinook salmon parr (*Oncorhynchus tshawytscha)* exposed to 120 µg/L chromium (Farag et al., 2006). Farag et al. (2003) documented the mortality of fish in sites

contaminated with cadmium, copper, and zinc. Fish death was linked to hypertrophy and degeneration of gill issue caused by waterborne metal exposure.

Salmonid olfaction is an important factor for migration, reproduction, and species identification. A recent review (Watershed Investigations Section, 2005) of the effects of copper on salmonid olfaction found the following: (1) Giattina et al. (1982) reported that salmonids appear to exhibit avoidance behavior at very low (1.4 to 7 µg/L) copper levels; (2) moderate concentrations of copper inhibit olfactory responses to certain important odors (Hansen et al., 1999a); and (3) at elevated copper levels (44 to 390 µg/L), olfactory nerves fail to identify and thus avoid potentially lethal levels of copper (Hansen et al., 1999a; Giattina et al., 1982). In more recent work, Sandahl et al. (2007) documented predator avoidance behaviors of juvenile coho that were significantly impaired by copper at concentrations as low as 2 µg/L.

In summary, metals can be taken up by fish across their gut from the diet or across their gills from the water. The gills and gut are the organs most directly affected by either of these routes. Trace metals can be measured in other organs within hours of exposure, and toxic effects can occur within days. Fish can regulate metal exposure and absorption by avoiding metal-contaminated water and by production of metallothionein. However, these responses have indirect effects on the physiology and growth of individuals and can force limitations on habitat and food availability in populations. The effects of metals can be measured as changes in fish physiology (metallothionein), sublethal effects (reduced growth and reproduction), and survival (direct toxicity). Measuring these effects simultaneously, in naturally contaminated sites, is the best way to document the toxic effects of trace metals on fish (Farag et al., 2003).

Assimilation of Metals by Piscivorous Vertebrates

Trace metals that have accumulated in fish can be transferred to, and affect, piscivorous wildlife. In the Yukon River, Alaska, mercury, selenium, and zinc exceeded toxicity thresholds for fish, and mercury was considered a risk for Alaskan fish and wildlife (Hamilton, 2004; Hinck et al., 2006). Mercury converts to methylmercury in anoxic environments (e.g., lake or wetland sediments) and bioaccumulates readily. Therefore, it may be particularly prone to accumulation in piscivorous wildlife (Hill et al., 1996; Scheuhammer et al., 2007). The majority of mercury deposition in the Arctic is deposited from long-range anthropogenic sources (e.g., coal-fired power plants; Poissant et al., 2008). However, short-range anthropogenic sources (e.g., mining) should be considered, particularly where lakes or other methylation environments occur. Methylation is the bonding of methyl group(s) to metals or metalloids, affecting solubility and mobility. Methylation of mercury and arsenic has been documented as major factors in the environmental movement of these elements (Thayer, 2004).

Trophic Transfer and Community-Level Effects of Metals in Aquatic Systems

It is important to take a holistic look at ways that trace metals can affect an ecosystem. Metals can be taken up at one trophic level and then transferred to other levels (Fisher and Hook, 2002). The transfer and bioaccumulation of metals associated with mining has been documented in the Coeur d'Alene River Basin, Idaho (Farag et al., 1999), the Animas River, Colorado (Church et al., 2007), and the Boulder River Basin, Montana (Farag et al., 2007). Generally, the trend in metal transfer is from biofilm to macroinvertebrates to fish. Most coldwater systems have relatively simple trophic structures that can be conceptualized linearly. That is, metals are transferred from primary producers through invertebrates and insectivorous fish to top predators. However, when appropriate, it is important to consider trace metal transfer in the context of a food web (Croteau et al., 2005). Trace metals may be transferred most directly,

and accumulate more rapidly, in insectivorous fish or birds rather than piscivorous fish (Chen and Folt, 2000).

Metals can also cause shifts in community structure that can indirectly affect other trophic levels. For example, trace metals could change the dominant biofilm species, changing invertebrate food availability and shifting the dominant invertebrate species. In this scenario, metals did not affect invertebrates directly, but the effects of metals changed the dominant invertebrate species indirectly by changing the dominant biofilm species.

Useful Tools in Studies of Trace Metals

Concentration of trace metals reported to affect aquatic animals varies widely in the literature. Dissolved organic matter, other dissolved ions, and pH cause variation in the bioavailability and the absorption rate of trace metals. For example, toxic levels of copper at 1 pH may have no effect at a different pH because its uptake by the organism is reduced (e.g., Meyer et al., 1999). Early attempts to reconcile these differences resulted in development of the free-ion activity model (FIAM) to explain toxic effects based on metal species and interactions with the organism. In addition, the gill surface interaction model (GSIM) was developed to account for the competition between water hardness cations and metal species for binding sites (e.g., gills). The FIAM and GSIM were linked in the biotic ligand model (BLM) by establishing the connection between toxic effects and the accumulated dose taken up at binding sites (ligands; Paquin et al., 2000). The BLM uses three separate components: (1) solution chemistry, (2) binding of the toxic metal to the ligand, and (3) accumulation of a toxic dose. The full model calculates toxic effects for a variety of scenarios. Changes in water chemistry, metal species, and organism species all affect the toxic dose. The BLM is able to account for these changes and predict the aquatic concentration at which metals will be toxic. The BLM was developed originally for fish, although it has been applied successfully to other aquatic organisms (Vijver et al., 2004).

Although the BLM has simplified and standardized the regulatory framework for establishing water quality criteria for metal contamination, three critical limitations exist. First, the BLM only considers metal availability from water across the gills. Although this is an important component of an organism's total metal exposure, dietary metal input often exceeds waterborne concentration. Incorporating dietary uptake is an important and necessary advancement of the BLM (Paquin et al., 2002). Second, the BLM only models acute exposure. Physiological changes that occur in animals during chronic exposure (e.g., increase in metallothionein production) change the internal processing of metals. The BLM models cannot account for these changes. Third, the BLM models use death as the endpoint. The model does not consider sublethal effects on an organism's growth or reproduction. While the BLM is an important tool for standardizing toxicity criteria for metals, separate models must be established for each potential metal and species combination (e.g., De Schamphelaere and Janssen, 2004). Models for even the most common metal and species combinations have yet to be established. The full utility of biodynamics models will not be realized until the full suite of models is established (Paquin et al., 2000). Until then, biodynamics models can be very useful in conceptualizing the reasons that metal accumulation varies by metal, species, and environment (Luoma and Rainbow, 2005).

Conclusions

1. Metals can be both essential and toxic to biotic receptors; the range in concentration between essentiality and toxicity can be very narrow or quite broad.

2. Human activities can change their natural cycles and redistribute them in various compartments of natural systems (Nriagu and Pacyna, 1988; Nriagu, 1990).
3. The geochemical environment influences the metal concentrations found in the surrounding ecosystem (Chang and Page, 1996).
4. Bioavailability and toxicity are controlled by speciation and physiochemical forms of metals in air, water, soil, and sediment (Jenne and Luoma, 1977).
5. Chemical, biological, and physical processes have a strong and complex influence on the speciation of metals and their subsequent behavior and mobility in the environment (Smith and Huyck, 1999).
6. Copper and zinc are essential at low levels to biofilms, invertebrates, and fish, but higher levels of these metals and other trace metals are toxic to these organisms.
7. Metals are actively taken into organisms, and their levels can be modestly regulated through sequestration.
8. Concentrations of metals in water can vary hourly, and concentrations in sediments can vary spatially throughout a floodplain.
9. Trace metals affect the abundance and diversity of biofilm, invertebrates, fish, and piscivorous wildlife by altering fundamental biological pathways.
10. Trace metals can be transferred among trophic levels and have community-wide effects.

References and Suggested Reading

Adriano, D.C., 1986. Trace Elements in Terrestrial Environment. Springer-Verlag, GmbH, 533 pp.

Adriano, D.C., 2001. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals, 2nd ed. Springer-Verlag, New York, 867 pp.

Agency for Toxic Substances and Disease Registry, 2003. Health Consultation: Selenium in Fish Streams of the Upper Blackfoot River Watershed, Southeast Idaho Selenium Project, Soda Springs, Idaho. Bureau of Environmental Health and Safety Division of Health, Idaho Department of Health and Welfare, under a cooperative agreement with the ATSDR.

Ainsworth, N., Cooke, J.A., and Johnson, M.S., 2004. Biological significance of antimony in contaminated grassland. Water, Air, and Soil Pollution, vol. 57–58, no. 1, pp. 193–197.

American Petroleum Institute, 1998. Arsenic: Chemistry, Fate, Toxicity, and Wastewater Treatment Options. Publication 4676. Health and Environmental Sciences Department, API, Washington, DC.

Arnon, D.I., and Stout, P.R., 1939. Molybdenum as an essential element for plants. Plant Physiology, vol. 14, pp. 599–602.

Athikesavan, S., Vincent, S., Ambrose, T., and Velmurugan, B., 2006. Nickel induced histopathological changes in the different tissues of freshwater fish *Hypophthalmichthys molitrix* (Valenciennes). Journal of Environmental Biology, vol. 37, no. 2, pp. 391–395.

August, E.E., McKnight, D.M., Hrncir, D.C., and Garhart, K.S., 2002. Seasonal variability of metals transport through a wetland impacted by mine drainage in the Rocky Mountains. Environmental Science

and Technology, vol. 36, no. 17, pp. 3779–3786.

Axtmann, E.V., Cain, D.J., and Luoma, S.N., 1997. Effect of tributary inflows on distribution of trace metals in fine-grained bed sediments and benthic insects of the Clark Fork River, Montana. Environmental Science and Technology, vol. 31, pp. 750–758.

Bailey, E.A., and Gray, J.E., 1997. In: Geologic Studies in Alaska by the U.S. Geological Survey, 1995, J.A. Dumoulin, and J.E. Gray, eds. USGS Professional Report 1574. U.S. Geological Survey, Reston, VA.

Behra, D.R., 2000. Long-term effects of copper on the structure of freshwater periphyton communities and their tolerance to copper, zinc, nickel, and silver. Aquatic Toxicology, vol. 47, pp. 181–189.

Beltman, D.J., Clements, W.H., Lipton, J., and Cacela, D., 1999. Benthic invertebrate metals exposure, accumulation, and community-level effects downstream from a hard-rock mine site. Environmental Toxicology and Chemistry, vol. 18, pp. 299–307.

Besser, J.M., and Brumbaugh, W.G., 2007. Status of stream biotic communities on relation to metal exposure. In: Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed, San Juan County, Colorado, S.E. Church, P. von Guerard and S.E. Finger, eds. U.S. Geological Survey, Reston, VA.

Besser, J.M., Brumbaugh, W.G., May, T.W., Church, S.E., and Kimball, B.A., 2001. Bioavailability of metals in stream food webs and hazards to brook trout (*Salvelinus fontinalis*) in the upper Animas River watershed, Colorado. Archives of Environmental Contamination and Toxicology, vol. 40, pp. 48–59.

Beyer, W.N., and Storm, G., 1995. Handbook of Ecotoxicology. CRC Press, Boca Raton, FL.

Beyer, W.N., Pattee, O.H., Sileo, L., Hoffman, D.J., and Mulhern, B.M., 1985. Environmental Pollution, vol. 38, pp. 63–86.

Bloom, N., 1992. Canadian Journal of Fisheries and Aquatic Sciences, vol. 49, pp. 1010–1017.

Boivin, M.E.Y., Massieux, B., Breure, A.M., van den Ende, F.P., Greve, G.D., Rutgers, M., and Admiraal, W., 2005. Effects of copper and temperature on aquatic bacterial communities. Aquatic Toxicology, vol. 71, pp. 345–356.

Boivin, M.-E.Y., Massieux, B., Breure, A.M., Greve, G.D., Rutgers, M., and Admiraal, W., 2006. Functional recovery of biofilm bacterial communities after copper exposure. Environmental Pollution, vol. 140, pp. 239–246.

Boudou, A., Maury-Brachet, R., Coquery, M., Durrieux, G., and Cossa, D., 2005. Synergic effect of goldmining and damming on mercury contamination in fish. Environmental Science and Technology, vol. 39, pp. 2448–2454.

Bowie, S.H.U., and Thornton, I., eds., 1985. Environmental Geochemistry and Health. Kluwer Academic, Hingham, MA.

Buchwalter, D.B., Cain, D.J., Clements, W.H., and Louma, S.N., 2007. Using biodynamic models to reconcile differences between laboratory toxicity tests and field biomonitoring with aquatic insects. Environmental Science and Technology, vol. 41, pp. 4821–4828.

Bury, N.R., 2005. The changes to apical silver membrane uptake, and basolateral membrane silver export

in the gills of rainbow trout (*Oncorhynchus mykiss*) on exposure to sublethal silver concentrations. Aquatic Toxicology, vol. 72, no. 1–2, pp. 135–145.

Bury, N.R., Walker, P.A., and Glover, C.N., 2003. Nutritive metal uptake in teleost fish. Journal of Experimental Biology, vol. 206, pp. 11–23.

Cain, D.J., Carter, J.L., Fend, S.V., Louma, S.N., Alpers, C.N., and Taylor, H.E., 2000. Metal exposure in a benthic macro invertebrate, *Hydropsyche californica*, related to mine drainage in the Sacramento River. Canadian Journal of Fisheries and Aquatic Sciences, vol. 57, pp. 380–390.

Cain, D.J., Louma, S.N., and Wallace, W.G., 2004. Linking metal bioaccumulation of aquatic insects to their distribution patterns in a mining-impacted river. Environmental Toxicology and Chemistry, vol. 23, pp. 1463–1473.

Cain, D.J., Buchwalter, D.B., and Louma, S.N., 2006. Influence of metal exposure history on the bioaccumulation and subcellular distribution of aqueous cadmium in the insect *Hydropsyche californica*. Environmental Toxicology and Chemistry, vol. 25, pp. 1042–1049.

Callahan, M.A., Slimak, M.W., and Gabel, N.W., 1978. Water-Related Environmental Fate of 129 Priority Pollutants, vol. 1. EPA 440/4-79-029. Office of Water Planning and Standards, U.S. Environmental Protection Agency, Washington, DC.

Campbell, P.G.C., Giguère, A., Bonneris, E., and Hare, L., 2005. Cadmium-handling strategies in two chronically exposed indigenous freshwater organisms, the yellow perch (*Perca flavescens*) and the floater mollusc (*Pyganodon grandis*). Aquatic Toxicology, vol. 72, pp. 83–97.

Camusso, M., Viganò, L., and Balestrini, R., 1995. Bioconcentration of trace metals in rainbow trout: a field study. Ecotoxicology and Environmental Safety, vol. 31, pp. 133–141.

Canadian Council of Ministers of the Environment, 1996. Recommended Canadian Soil Quality, Guidelines for Arsenic: Environmental and Human Health, Supporting Document—Final Draft. CCME, Ottawa, ON, Canada.

Carlisle, D.M., and Clements, W.H., 1999. Sensitivity and variability of metrics used in biological assessments of running waters. Environmental Toxicology and Chemistry, vol. 18, pp. 285–291.

Chang, A.C., and Page, A.L., 1996. Assessment of ecological and health effects of soil-borne trace elements and metals. In: Toxicity of Metals, L.W. Chang, ed. CRC Press, Boca Raton, FL.

Cheam, V., 2001. Thallium contamination of water in Canada, Water Quality Research Journal of Canada, vol. 36, no. 4, pp. 851–877.

Chen, C.Y., and Folt, C.L., 2000. Bioaccumulation and diminution of arsenic and lead in a freshwater food web. Environmental Science and Technology, vol. 34, pp. 3878–3884.

Christensen, J.W., 1991. Global Science. Kendall/Hunt, Dubuque, IA, 269 pp.

Church, S.E., Owen, J.R., von Guerard, P., Verplanck, P.L., Kimball, B.A., and Yager, D.B., 2007. The effects of acidic mine drainage from historical mines in the Animas River watershed, San Juan County, Colorado: What is being done and what can be done to improve water quality? In: Understanding and Responding to Hazardous Substances at Mine Sites in the Western United States, J.V. DeGraff, ed. Geological Society of America Reviews in Engineering Geology, vol. XVII, pp. 47–83.

Clearwater, S.J., Baskin, S.J., Wood, C.M., and McDonald, D.G., 2000. Gastrointestinal uptake and distribution of copper in rainbow trout. Journal of Experimental Biology, vol. 2003, pp. 2455–2466.

Clearwater, S.J., Farag, A.M., and Meyer, J.S., 2002. Bioavailability and toxicity of dietborne copper and zinc to fish. Comparative Biochemistry and Physiology, vol. 132, pp. 269–313.

Clements, W.H., 1994. Benthic invertebrate community responses to heavy metals in the Upper Arkansas River Basin, Colorado. Journal of the North American Benthological Society, vol. 13, pp. 30–44.

Clements, W.H., 2004. Small-scale experiments support causal relationships between metal contamination and macroinvertebrate community responses. Ecological Applications, vol. 14, pp. 954–967.

Clements, W.H., and Kiffney, P.M., 1995. The influence of elevation on benthic community responses to heavy metals in Rocky Mountain streams. Canadian Journal of Fisheries and Aquatic Sciences, vol. 52, pp. 1966–1977.

Clements, W.H., Carlisle, D.M., Lazorchak, J.M., and Johnson, P.C., 2000. Heavy metals structure benthic communities in Colorado mountain streams. Ecological Applications, vol. 10, pp. 626–638.

Croteau, M.-N., Luoma, S.N., and Stewart, A.R., 2005. Trophic transfer of metals along freshwater food webs: evidence of cadmium biomagnification in nature. Limnology and Oceanography, vol. 50, pp. 1511–1519.

Cullen, W.R., and Reimer, K.J., 1989. Arsenic speciation in the environment. Chemical Reviews ,vol. 89, pp. 713–764.

Dallinger, R., Prosi, F., Segner, H., and Back, H., 1987. Contaminated food and uptake of heavy metals by fish: a review and proposal of further research. Oecologia, vol. 73, pp. 91–98.

De Groot, A., Zshuppe, K., and Salomons, W., 1982. Standardization of methods of analysis for heavy metals in sediments. Hydrobiologia, vol. 92, pp. 689–695.

De Schamphelaere, K.A.C., and Janssen, C.R., 2004. Bioavailability and chronic toxicity of zinc to juvenile rainbow trout (*Oncorhynchus mykiss*): comparison with other fish species and development of a biotic ligand model. Environmental Science and Technology, vol. 38, pp. 6201–6209.

Eisler, R., 1985. Cadmium Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Geological Survey, Biological Resources Division, Biological Report 85(1.2). Patuxent Wildlife Research Center, U.S. Fish and Wildlife Service, Laurel, MD.

Eisler, R., 1986. Chromium Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Fish and Wildlife Service Biological Report 85 (1.6). Patuxent Wildlife Research Center, U.S. Fish and Wildlife Service, Laurel, MD.

Eisler, R., 1988. Lead Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Fish and Wildlife Service Biological Report 85(1.14). Patuxent Wildlife Research Center, U.S. Fish and Wildlife Service, Laurel, MD.

Eisler, R., 1996. Silver Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. Biological Report 32, Contaminant Hazard Reviews. Patuxent Wildlife Research Center, U.S. National Biological Service, Laurel, MD.

Eisler, R., 1998. Copper Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Geological Survey, Biological Resources Division, Biological Science Report USGS/BRD/BSR—1998-0002. Patuxent Wildlife Research Center, U.S. Fish and Wildlife Service, Laurel, MD.

Evans, R.D., Balch, G.C., Evans, H.E., and Welbourn, P.M., 2006. Uptake and elimination of lead zinc, and copper by caddisfly larvae (*Trichoptera Hydropsychidae*) using stable isotope tracers. Archives of Environmental Contamination and Toxicology, vol. 51, pp. 35–42.

Farag, A.M., Woodward, D.F., Brumbaugh, W.G., Goldstein, J.N., MacConnell, E., Hogstrand, C., and Barrows, F.T., 1999. Dietary effects of metals-contaminated invertebrates from the Coeur d'Alene River, Idaho, on cutthroat trout. Transactions of the American Fisheries Society, vol. 128, pp. 578–592.

Farag, A.M., Skaar, D., Nimick, D.A., MacConnell, E., and Hogstrand, C., 2003. Characterizing aquatic health using salmonid mortality, physiology, and biomass estimates in streams with elevated concentrations of arsenic, cadmium, copper, lead, and zinc in the Boulder River watershed, Montana. Transactions of the American Fisheries Society, vol. 132, pp. 450–467.

Farag, A.M., May, T., Marty, G.D., Easton, M., Harper, D.D., Little, E.E., and Cleveland, L., 2006a. The effect of chronic chromium exposure on the health of Chinook salmon (*Oncorhynchus tshawytscha*). Aquatic Toxicology, vol. 76, pp. 246–257.

Farag, A.M., Harper, D.D., Cleveland, L., Brumbaugh, W.G., and Little, E.E., 2006b. The potential for chromium to affect the fertilization process of Chinook salmon (*Oncorhynchus ishawytscha*) in the Hanford Reach of the Columbia River, Washington, USA. Archives of Environmental Contamination and Toxicology, vol. 50, pp. 575–579.

Farag, A.M., Nimick, D.A., Kimball, B.A., Church, S.E., Harper, D.D., and Brumbaugh, W.G., 2007. Concentrations of metals in water, sediment, biofilm, benthic macroinvertebrates and fish in the Boulder River watershed, Montana, and the role of colloids in metal uptake. Archives of Environmental Contamination and Toxicology, vol. 52, pp. 397–409.

Fernandes, J.C., and Henriques, F.S., 1991. Biochemical, physiological and structural effects of excess copper in plants. Botanical Review, vol. 57, pp. 246–273.

Fessler, A.L., Moller, G., Talcott, G.P.A., and Exon, J.H., 2003. Selenium toxicity in sheep grazing reclaimed phosphate sites. Veterinary and Human Toxicology, vol. 45, no. 6, pp. 294–298.

Finn, R.N., 2007. The physiology and toxicology of salmonid eggs and larvae in relation to water quality criteria. Aquatic Toxicology, vol. 81, pp. 337–354.

Fisher, N.S., and Hook, S.E., 2002. Toxicology tests with aquatic animals need to consider the trophic transfer of metals. Toxicology, vol. 181–182, 531–536.

Florence, T.M., and Batley, G.E., 1980. Critical Review Analytical Chemistry, vol. 59, pp. 291–302.

Fromm, P.O., 1980. A review of some physiological and toxicological responses of freshwater fish to acid stress. Environmental Biology of Fishes, vol. 5, no. 1, pp. 79–93.

Gadd, G.M., and Griffiths, A.J., 1978. Microorganisms and heavy metal toxicity. Microbial Ecology, vol. 4, pp. 303–317.

Gammons, C.H., Nimick, D.A., Parker, S.R., Cleasby, T.E., and McCleskey, R.B., 2005. Diel behavior of

iron and other heavy metals in a mountain stream with acid and neutral pH, Fisher Creek, Montana, USA. Geochimica et Cosmochimica Acta, vol. 69, no. 10, pp. 2505–2516.

Giattina, J.D., Garton, R.R., and Stevens, D.G., 1982. Avoidance of copper and nickel by rainbow trout as monitored by a computer-based data acquisition system. Transactions of the American Fisheries Society, vol. 111, pp. 491–504.

Gibbs, R., 1977. Transport phases of transition metals in the Amazon and Yukon rivers. Geological Society of America Bulletin, vol. 88, pp. 829–843.

Giddings, E.M., Hornberger, M.I., and Hadley, H.K., 2001. Trace-Metal Concentrations in Sediment and Water Health of Aquatic Macroinvertebrate Communities of Streams near Park City, Summit County, Utah. U.S. Geological Survey, Salt Lake City, UT.

Giguère, A., Campbell, P.G.C., Hare, L., and Cossu-Leguille, C., 2005. Metal bioaccumulation and oxidative stress in yellow perch (*Perca flavescens*) collected from eight lakes along a metal contamination gradient (Cd, Cu, Zn, Ni). Canadian Journal of Fisheries and Aquatic Sciences, vol. 62, pp. 563–577.

Glover, C.N., and Hogstrand, C., 2003. Effects of dissolved metals and other hydrominerals on in vivo intestinal zinc uptake in freshwater rainbow trout. Aquatic Toxicology, vol. 62, no. 4, pp. 281–293.

Goodyear, K.L., and McNeill, S., 1999. Bioaccumulation of the heavy metals by aquatic macro-invertebrates of different feeding guilds: a review. Science of the Total Environment, vol. 229, pp. 1–19.

Graf, W.L., Clark, S.L., Kammerer, M.T., Lehman, T., Randall, K., and Schroeder, R., 1991. Geomorphology of heavy metals in the sediments of Queen Creek, Arizona, USA. Catena, vol. 18, no. 6, pp. 567–582.

Guasch, H., Paulsson, M., and Sabater, S., 2002. Effect of copper on algal communities from oligotrophic calcareous streams. Journal of Phycology, vol. 38, pp. 241–248.

Hambidge, K.M., Casey, C.E., and Krebs, N.F., 1986. Trace Elements in Human and Animal Nutrition, 5th ed. Academic Press, Orlando, FL.

Hamilton, S.J., 2004. Review of selenium toxicity in the aquatic food chain. Science of the Total Environment, vol. 326, pp. 1–31.

Handy, R.D., McGeer, J.C., Allen, H.E., Drevnick, P.E., Gorsuch, J.W., Green, A.S., et al., 2003. Toxic effects of dietborne metals: laboratory studies. In: Toxicity of dietborne metals to aquatic organisms. J.S. Meyer, et al., eds. Society of Environmental Toxicology and Chemistry (SETAC). Pensacola, FL.

Hansen, J.A., Rose, J.D., Jenkins, R.A., Gerow, K.G., and Bergman, H.L., 1999a. Chinook salmon (*Oncorhynchus tshawytscha*) and rainbow trout (*Oncorhynchus mykiss*) exposed to copper: neurophysiological and histological effects on the olfactory system. Environmental Toxicology and Chemistry, vol. 18, no. 9, pp. 1979–1991.

Hansen, J.A., Marr, J.C.A., Lipton, J., Cacela, D., and Bergman, H.L., 1999b. Differences in neurobehavioral responses of Chinook salmon (*Oncorhynchus tshawytscha*) and rainbow trout (*Oncorhynchus mykiss*) exposed to copper and cobalt: behavioral avoidance. Environmental Toxicology and Chemistry, vol. 18, no. 9, pp. 1972–1978.

Hansen, J.A., Woodward, D.F., Little, E.E., DeLonay, A.J., and Bergman, H.L., 1999c. Behavioral avoidance: possible mechanism for explaining abundance and distribution of trout species in a metal-impacted river. Environmental Toxicology and Chemistry, vol. 18, pp. 313–317.

Hansen, J.A., Welsh, P.G., Lipton, J., and Cacela, D., 2002. Effects of copper exposure on growth and survival of juvenile bull trout. Transactions of the American Fisheries Society, vol. 131, pp. 690–697.

Hare, L., 1992. Aquatic insects and trace metals: bioavailability, bioaccumulation and toxicity. Critical Reviews in Toxicology vol. 22, pp. 327–369.

Hart, B.T., 1982. Sediment–freshwater interaction. In: Developments in Hydrobiology, P.G., Sly, ed. The Hague, Netherlands.

Hausinger, R.P., 1992. In: Nickel and Human Health, E. Nieboer and J.O. Nriagu, eds. Wiley, New York.

Henny, C.J., 2003. Effects of mining lead on birds: a case history at Couer d'Alene Basin, Idaho. In: Handbook of Ecotoxicology, D.J. Hoffman, B.A. Rattner, and G.A. Burton, Jr., eds. CRC Press, Boca Raton, FL.

Hewitt, E.J., and Smith, T.A., 1974. Plant Mineral Nutrition. English University Press, London.

Hill, R.D., 1974. Mining impacts on trout habitat. Proceedings of a Symposium on Trout Habitat, Research, and Management. Appalachian Consortium Press, Boone, NC.

Hill, W.R., Stewart, A.J., and Napolitano, G.E., 1996. Mercury speciation and bioaccumulation in lotic primary producers and primary consumers. Canadian Journal of Fisheries and Aquatic Sciences, vol. 53, pp. 812–819.

Hill, W.R., Bednarek, A.T., and Larsen, I.L., 2000. Cadmium sorption and toxicity in autotrophic biofilms. Canadian Journal of Fisheries and Aquatic Sciences, vol. 57, pp. 530–537.

Hinck, J.E., Schmit, C.J., Echols, K.R., May, T.W., Orazio, C.E., and Tillitt, D.E., 2006. Environmental contaminants on fish and their associated risk to piscivorous wildlife in the Yukon river Basin, Alaska. Archives of Environmental Contamination and Toxicology, vol. 51, pp. 661–672.

Hodson, P.V., 1988. The effect of metal metabolism on uptake disposition and toxicity in fish. Aquatic Toxicology, vol. 11, pp. 3–18.

Hoffman, D.J., 2002. Role of selenium toxicity and oxidative stress in aquatic birds. Aquatic Toxicology, vol. 57, no. 102, pp. 11–26.

Holdgate, M.W., ed., 1971. The Seabird Wreck of 1969 in the Irish Sea. Natural Environment Research Council, London.

Holding, K.L., Gill, R.A., and Carter, J., 2003. The relationship between epilithic periphyton (biofilm) bound metals and metals bound to sediments in freshwater systems. Environmental Geochemistry and Health, vol. 25, pp. 87–93.

Hopkin, S.P., 1989. Ecophysiology of Metals in Terrestrial Invertebrates. Elsevier Applied Science, Amsterdam, 366 pp.

Huang, Y.-C., 1994. Arsenic distribution in soils. In: Arsenic in the Environment, Part I, Cycling and

Characterization, J.O. Nriagu ed. Wiley, New York, pp. 17–49.

Jagoe, C.H., Matey, V.E., Haines, T.A., and Komov, V.T., 1993. Effect of beryllium in acid water is analogous to aluminum toxicity. Aquatic Ecology, vol. 24, pp. 241–256.

Jaworski, J.F., ed., 1980. Executive Reports: Effects of Chromium, Alkali Halides, Arsenic, Mercury, and Cadmium in the Canadian Environment. NRCC No. 17585. National Research Council of Canada, Ottawa, ON, Canada.

Jenne, E.A., and Luoma, S.N., 1997. Forms of trace elements in soils, sediments and associated waters: an overview of their determination and biological availability. In: Biological Implications of Metals in the Environment, R.E. Wildung, and H. Drucker, eds. Energy Research and Development Administration Symposium Series 42. Technical Information Center, Springfield, VA.

Jones, C.A., Nimick, D.A., and McCleskey, R.B., 2004. Relative effect of temperature and pH on diel cycling of dissolved trace elements in Prickly Pear Creek, Montana. Water Air and Soil Pollution, vol. 153, pp. 95--113.

Julia-Laurence, C., Aurélie, F., Serge, C., Mori, C., and Orsini, A., 2009. Trophic transfer of arsenic and antimony in a freshwater ecosystem: a field study. Aquatic Toxicology, vol. 94, pp. 286–293.

Kabata-Pendias, A., 1993. Behavioral properties of trace metals in soils. Applied Geochemistry, suppl, vol. 2, pp. 3.

Kabata-Pendias, A., 2001. Trace Elements in Soils and Plants, 3rd ed., CRC Press, Boca Raton, FL, 413 pp.

Kelly, M., 1988. Mining and the Freshwater Environment. Elsevier Science, London.

Kimmel, W.G., 1983. The impact of acid mine drainage on the stream ecosystem. In: Pennsylvania Coal: Resources, Technology, and Utilization, S.J. Majumdar and E.W. Willard, eds. Pennsylvania Academy of Science, Bradford, PA, pp. 424–437.

Kochian, L.V., 1993. In: Zinc in Soils and Plants, A.D. Robson, ed. Kluwer, Academic, Dordrecht, The Netherlands.

Krauskopf, K.B., 1979. Introduction to Geochemistry, 2nd ed. McGraw-Hill, New York.

Lacerda, L.D., Bidone, E.D., Guimaraes, A.F., and Pfeiffer, W.C., 1994. Annals of the Academy of Brazil, vol. 66, pp. 373–379.

Ladd, S.C., Marcus, W.A., and Cherry, S., 1998. Differences in trace metal concentrations among fluvial morphologic units and implications for sampling. Environmental Geology, vol. 36, pp. 259–270.

Langard, S., and Norseth, T., 1979. Chromium. Pages 383–397 In: Handbook on the Toxicology of Metals, L. Friberg, G.F. Nordberg, and V.B. Vouk, eds. Elsevier/North-Holland Biomedical Press, Amsterdam.

Langston, W.J., and Spence, S.K., 1995. Biological factors involved in metal concentrations observed in aquatic organisms. In: Metal Speciation and Bioavailability in Aquatic System, A. Tessier and D.R. Turner, eds. Wiley, Chichester, UK, pp. 407–478.

Lanno, R.P., Slinger, S.J., and Hilton, J.W., 1985. Maximum tolerable and toxicity levels of dietary copper in rainbow trout (*Salmo gairdneri* Richerdson). Aquaculture, vol. 49, pp. 257–268.

Larison, J.R., Likens, G.E., Fitzpatrick, J.W., and Crock, J.R., 2000. Cadmium toxicity among wildlife in the Colorado Rocky Mountains. Nature, vol. 405, pp. 181–183.

Likens, G.E., Bormann, F.H., Pierce, R.S., Eaton, J.S., and Johnson, N.M., 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York.

Logan, T.J., and Traina, S.J., 1993. In: Metals in Groundwater. H.E. Allen et al., eds. Lewis Publishers/SRC Press, Boca Raton, FL.

Luoma, S.N., and Phillips, D.J.H., 1988. Distribution, variability, and impacts of trace elements in San Francisco Bay. Marine Pollution Bulletin, vol. 19, pp. 413–425.

Luoma, S.N., and Rainbow, P.S., 2005. Why is metal bioaccumulation so variable? Biodynamics as a unifying concept. Environmental Science and Technology, vol. 39, pp. 1921–1931.

Madejon, P., Moranon, J., Murillo, J.M., and Robinson, B., 2004. White poplar (*Populus alba*) as a biomonitor of trace elements in contaminated riparian forests. Environmental Pollution, vol. 132, pp. 145–155.

Maher, W., 1986. Measurement of total antimony in marine organisms and waters by stibine generation and atomic absorption spectrometry. Analytical Letters, vol. 19, pp. 295–305.

Maltby, L., 1999. Studying stress: the importance of organism-level responses. Ecological Applications, vol. 9, pp. 31–440.

Mance, G., 1987. Pollution Threats of Heavy Metals in Aquatic Environments. Elsevier, London.

Marcus, W.A., Meyer, G.A., and Nimmo, D.R., 2001. Geomorphic control of persistent mine impacts in a Yellowstone Park stream and implications of the recovery of fluvial systems. Geology, vol. 29, pp. 355–358.

Maret, T.R., and MacCoy, D.E., 2002. Fish assemblages and environmental variables associated with hard-rock mining in the Coeur d'Alene River Basin, Idaho. Transactions of the American Fisheries Society, vol. 131, pp. 865–884.

Maret, T.R., Cain, D.J., MacCoy, D.E., and Short, T.M., 2003. Response of benthic invertebrate assemblages to metal exposure and bioaccumulation associated with hard-rock mining in northwestern streams, USA. Journal of the North American Benthological Society, vol. 22, pp. 598–620.

Mason, A.Z., and Jenkins, K.D., 1995. Metal detoxification in aquatic organisms. In: Metal Speciation and Bioavailability in Aquatic Systems, vol. 3, A. Tessier and D.R. Turner eds. Wiley, Chichester, UK, pp. 479–608.

Mason, R.P., Fitzgerald, W.F., and Morel, F.M.M., 1994. The biogeochemistry of elemental mercury: anthropogenic influences. Geochimica et Cosmochimica Acta, vol. 58, pp. 3191–3198.

Massieux, B., Boivin, M.E.Y., Ende, F.P.v.d., Langenskiöld, J., Marvan, P., Barranguet, C., Admiraal, W., Laanbroek, H.J., and Zwart, G., 2004. Analysis of structural and physiological profiles to assess the effects of Cu on biofilm microbial communities. Applied and Environmental Microbiology, vol. 70,

pp. 4512–4521.

McKnight, D.M., and Hrncir, D., 2001. Final Report: Photochemical Processes Controlling Manganese Chemistry in Pristine and Contaminated Mountain Streams. Region 8, Final Report R826649. U.S. Environmental Protection Agency, Washington, DC.

Meyer, J.S., Santore, R.C., Bobbitt, J.P., Debrey, L.D., Boese, C.J., Paquin, P.R., Allen, H.E., Bergman, H.L., and Di Toro, D.M., 1999. Binding of nickel and copper to fish gills predicts toxicity when water hardness varies, but free-ion activity does not. Environmental Science and Technology, vol. 33, pp. 913–916.

Meyer, J.S., Adams, W.J., Brix, K.V., Luoma, S.N., Mount, D.R., Stubblefield, W.W., and Wood, C.M., 2005. Toxicity of Dietborne Metals to Aquatic Organisms. SETAC Press, Pensacola, FL.

Meylan, S., Behra, D.R., and Sigg, L., 2003. Accumulation of copper and zinc in periphyton in response to dynamic variations of metal speciation in freshwater. Environmental Science and Technology, vol. 37, pp. 5204–5212.

Meylan, S., Behra, R., and Sigg, L., 2004. Influence of metal speciation in natural freshwater on bioaccumulation of copper and zinc in periphyton: a microcosm study. Environmental Science and Technology, vol. 38, pp. 3104–3111.

Miller, J.R., 1997. The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites. Journal of Geochemical Exploration, vol. 58, pp. 101–118.

Moore, J.W., 1991. Inorganic Contaminants in Surface Water. Springer-Verlag, New York.

Morin, S., Duong, T.T., Herlory, O., Feurtet-Mazel, A., and Coste, M., 2008. Cadmium toxicity and bioaccumulation in freshwater biofilms. Archives of Environmental Contamination and Toxicology, vol. 54, pp. 173–186.

Morris, J.M., Farag, A.M., Nimick, D.A., and Meyer, J.S., 2006. Light-mediated Zn uptake in photosynthetic biofilm. Hydrobiologia, vol. 571, pp. 361–371.

Munshower, F.F., and Neuman, D.R., 1979. Metals in soft tissues of mule deer and antelope. Bulletin of Environmental Contamination and Toxicology, vol. 22, pp. 827–832.

National Academy of Sciences, 1999. Measuring Lead Exposure in Infants, Children, and Other Sensitive Populations. National Academies Press, Washington, DC.

National Association of Photographic Manufacturers, 1974. Environmental Effect of Photoprocessing Chemicals, vols. I and II. NAPM, Harrison, NY, 324 pp. plus appendixes.

National Research Council, 2005. Mineral Tolerance of Animals, 2nd Rev. ed. National Academies Press, Washington, DC, 496 pp.

Nebeker, A.V., McAuliffe, C.K., Mshar, R., and Stevens, D.G., 1983. Toxicity of silver to steelhead and rainbow trout, fathead minnows and *Daphnia magna*. Environmental Toxicology and Chemistry, vol. 2, pp. 95–104.

Neuman, D.R., and Dollhopf, D.J., 1992. Lead levels on blood from cattle residing near a lead smelter. Journal of Environmental Quality, vol. 21, pp. 181–184.

Neuman, D.R., Brown, P., Jackson, D., and Jennings, S.R., 2009. Metals: Freshwater Fish Health and Ecology—A Literature Review. Reclamation Research Group Publication, Bozeman, MT, 73 pp.

Newman, M.C., and McIntosh, A.W., 1989. Appropriateness of aufwuchs as a monitor of bioaccumulation. Environmental Pollution, vol. 60, pp. 83–100.

Newman, M.C., and Unger, M.A., 2003. Fundamentals of Ecotoxicology, 2nd ed. CRC Press, Lewis Publishers/Boca Raton, FL, 458 pp.

Nimick, D.A., Cleasby, T.E., and McCleskey, R.B., 2005. Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky Mountain stream. Environmental Geology, vol. 47, pp. 603–614.

Nriagu, J.O., 1990. Global metal pollution. Environment, vol. 33, no. 6, pp. 28–33.

Nriagu, J.O., and Pacyna, J.M., 1988. Quantitative assessment of world wide contamination of air, water, and soils by trace metals. Nature, vol. 330, pp. 134–139.

Ohlendorf, H.M., 2002. The birds of Kesterson Reservoir: a historical perspective. Aquatic Toxicology, vol. 57, no. 1–2, pp. 1–10.

Olson, K.R., Squibb, K.S., and Cousins, R.J., 1978. Tissue uptake, subcellular distribution, and metabolism of $^{14}CH_3HgCl$ and $CH_3{}^{203}HgCl$ by rainbow trout, *Salmo gairdneri*. Journal of the Fisheries Research Board of Canada, vol. 35, no. 4, pp. 381–390.

Pagenkopf, G.K., Russo, R.C., and Thurston, R.V., 1974. Effect of complexation on toxicity of copper to fishes. Journal of the Fisheries Research Board of Canada, vol. 31, pp. 462–465.

Pain, D.J., 1995. In: Handbook of Ecotoxicity. D.J., Hoffman et al., eds. CRC Press/Lewis Publishers, Boca Raton, FL.

Pais, I., and Jones, J.B., Jr. 1997. Handbook of Trace Elements. CRC Press/St. Lucie Press, Boca Raton, FL, 223 pp.

Paquin, P.R., Santore, R.C., Wu, K.B., Kavvadas, C.D., and Di Toro, D.M., 2000. The biotic ligand model: a model of the acute toxicity of metals to aquatic life. Environmental Science and Policy, vol. 3, pp. S175–S182.

Paquin, P.R., Gorsuch, J.W., Apte, S., Batley, G.E., Bowles, K.C., Campbell, P.G.C., Delos, C.G., Di Toro, D.M., Dwyer, R.L., Galvez, F., Gensemer, R.W., Goss, G.G., Hogstrand, C., Janssen, C.R., McGeer, J.C., Naddy, R.B., Playle, R.C., Santore, R.C., Schneider, U., Stubblefield, W.A., Wood, C.M., and Wu, K.B., 2002. The biotic ligand model: a historical overview. Comparative Biochemistry and Physiology, vol. 133, pp. 3–35.

Pawlik, B., and Skowroński, T., 1994. Transport and toxicity of cadmium: its regulation in the cyanobacterium *Synechocystis Aquatilis*. Environmental and Experimental Botany, vol. 34, pp. 225–233.

Peplow, D., and Edmonds, R., 2005. The effects of mine waste contamination at multiple levels of biological organization. Ecological Engineering, vol. 24, pp. 101–119.

Phillips, D.J.H., 1995. The chemistries and environmental fates of trace metals and organochlorines in aquatic ecosystems. Marine Pollution Bulletin, vol. 31, pp. 193–200.

Poissant, L., Zhang, H.H., Canário, J., and Constant, P., 2008. Critical review of mercury fates and contamination in the arctic tundra ecosystem. Science of the Total Environment, vol. 400, pp. 173–211.

Preston, A.M., Dowdy, R.P., Preston, M.A., and Freeman, J.N., 1976. Effect of dietary chromium on glucose tolerance and serum cholesterol in guinea pigs. Journal of Nutrition, vol. 106, pp. 1391–1397.

Rainbow, P.S., 2002. Trace metal concentrations in aquatic invertebrates: Why and so what? Environmental Pollution, vol. 120, pp. 97–507.

Rainbow, P.S., 2007. Trace metal bioaccumulation: models, metabolic availability and toxicity. Environment International, vol. 33, pp. 576–582.

Rickwood, P.C., 1983. Crystal abundance, distribution, and crystal chemistry of the elements. In: Handbook of Exploration Geochemistry, vol. 3, Rock Geochemistry in Mineral Exploration, G.J.S. Govett, ed. Elsevier Scientific, Amsterdam, pp. 347–387.

Ripley, E.A., Redmann, R.E., and Crowder, A.A., 1996. Environmental Effects of Mining. CRC Press/St. Lucie Press, Boca Raton, FL, 356 pp.

Roesijadi, G., 1992. Metallothioneins in metal regulation and toxicity in aquatic animals. Aquatic Toxicology, vol. 22, pp. 81–114.

Rose-Janes, N.G., and Playle, R.C., 2000. Protection by two complexing agents, thiosulphate and dissolved organic matter, against the physiological effects of silver nitrate to rainbow trout (*Oncorhynchus mykiss*) in ion-poor water. Aquatic Toxicology, vol. 51, pp. 1–18.

Rosenfeld, I., and Beath, O.A., 1964. Selenium: Geobotany, Biochemistry, Toxicity, and Nutrition. Academic Press, New York, pp. 411.

Salomons, W., and Forstner, U., 1984. Metals in the Hydrosphere. Springer-Verlag, Berlin.

Sandahl, J.F., Baldwin, D.H., Jenkins, J.J., and Scholz, N.L., 2007. A sensory system at the interface between urban stormwater runoff and salmon survival. Environmental Science and Technology, vol. 41, no. 8, pp. 2998–3004.

Sandmann, G., and Böger, P., 1980a. Copper deficiency and toxicity in *Scenedesmus*. Pflanzenphysiologie, vol. 98, pp. 53–59.

Sandmann, G., and Böger, P., 1980. Copper-mediated lipid peroxidation processes in photosynthetic membranes. Plant Physiology, vol. 66, pp. 797–800.

Sandmann, G., and Böger, P., 1983. Enzymological function of heavy metals and their role in electron transfer processes of plants. In: Encyclopedia of Plant Physiology, new series, Physiological Plant Ecology III: Responses to Chemical and Biological Environment, vol. 12A, Springer-Verlag, Berlin, pp. 246–300.

Sappal, R., Burka, J., Dawson, S., and Kamunde, C., 2009. Bioaccumulation and subcellular partitioning of zinc in rainbow trout (*Oncorhynchus mykiss*): cross-talk between waterborne and dietary uptake. Aquatic Toxicology, vol. 91, pp. 281–290.

Scheuhammer, A.M., ed., 1991. Environmental pollution: pH related changes in metal biochemistry and effects on aquatic systems. Environmental Pollution, vol. 71, pp. 1–38.

Scheuhammer, A.M., Meyer, M.W., Sandheinrich, M.B., and Murray, M.W., 2007. Effects of environmental methylmercury on the health of wild birds, mammals, and fish. Ambio, vol. 36, pp. 12–18.

Schlekat, C.E., Kidd, K.A., Adams, W.J., Baird, D.J., Farag, A.M., Maltby, L., and Stewart, A.R., 2005. Toxic effects of dietborne metals: field studies. In: Toxicity of Dietborne Metals, J. Meyer, ed. SETAC Press, Pensacola, FL, pp. 113–152.

Serra, A., Corcoll, N., and Guasch, H., 2009. Copper accumulation and toxicity in fluvial periphyton: the influence of exposure history. Chemosphere, vol. 74, pp. 633–641.

Shacklette, H.T., and Boerngen, J.G., 1984. Element Concentrations in Soils and Other Surficial Materials of the Conterminous United States. U.S. Geological Survey Professional Paper 1270. USGS, Washington, DC, pp. 105.

Shacklette, H.T., Hamilton, J.C., Boerngen, J.G., and Bowles, J.M., 1971. Elemental Composition of Surficial Materials in the Conterminous United States. U.S. Geological Survey Professional Paper 574-C. USGS, Washington, DC, 39 pp.

Siegel, F.R., 2002. Environmental Geochemistry of Potentially Toxic Metals. Springer-Verlag, Berlin, 212 pp.

Sileo, L., and Beyer, W.N., 1985. Heavy metals in white-tailed deer (*Odocoileus virginianus*) living near a zinc smelter in Pennsylvania. Journal of Wildlife Diseases, vol. 21, no. 3, pp. 289–296.

Smith, K.S., 1999. Cadmium. In: Encyclopedia of Geochemistry, C.P. Marshall and R.W. Fairbridge, eds. Kluwer Academic, Dordrecht, The Netherlands, pp. 50–51.

Smith, K.S., and Huyck, H.L.O., 1999. An overview of the abundance, relative mobility, bioavailability, and human toxicity of metals. In: The Environment of Geochemistry of Mineral Deposits, G.S. Plumlee and M.J. Logsdon, eds. Reviews in Economic Geology. Society of Economic Geologists, Littleton, Co.

Soldo, D., and Behra, R., 2000. Long-term effects of copper on the structure of freshwater periphyton communities and their tolerance to copper, zinc, nickel and silver. Aquatic Toxicology, vol. 47, pp. 181–189.

Spear, P.A., and Pierce, R.C., 1979. Copper in the Aquatic Environment: Chemistry, Distribution and Toxicology. No. 16454. National Research Council of Canada, Ottawa, ON, Canada.

Spehar, R.L., Anderson, R.L., and Fiandt, J.T., 1978. Toxicity and bioaccumulation of cadmium and lead in aquatic invertebrates. Environmental Pollution, vol. 15, pp. 195–208.

Stewart, A.J., Hill, W.R., and Boston, H.L., 1993. Grazers periphyton and toxicant movement in streams. Environmental Toxicology and Chemistry, vol. 12, pp. 955–957.

Stewart, A.R., Saiki, M.K., Kuwabara, J.S., Alpers, C.N., Marvin-DiPasquale, M., and Krabbenhoft, D.P., 2008. Influence of plankton mercury dynamics and trophic pathways on mercury concentration of top predator fish of a mining-impacted reservoir. Canadian Journal of Fisheries and Aquatic Sciences, vol. 65, pp. 2351–2366.

Stokes, P.M., 1979. Copper accumulations in freshwater biota. In: Copper in the Environment, Part 1. J.O. Nriager, ed. Wiley, New York, pp. 357–381.

Storm, G.L., Fosmire, G.J., and Bellis, E.D., 1994. Journal of Environmental Quality, vol. 23, pp. 508–514.

Sunda, W., 1989. Trace metal interactions with marine phytoplankton. Biological Oceanography, vol. 6, pp. 411–442.

Swaine, D.J., 1955. The Trace Element Content of Soils. Commonwealth Bureau of Soil Science (Great Britain), Technical Communication 48. Herald Printing Works, York, UK.

Swain, D.J., 1978. Journal of the Royal Society of New South Wales, vol. 111, pp. 41–47.

Thayer, J.S., 2004. Methylation: its role in the environmental mobility of heavy elements. Applied Organometallic Chemistry, vol. 3, no. 2, pp. 123.

Thurman, E.M., 1985. Organic Geochemistry of Natural Waters. Martius Nijhoff/Dr. W. Junk Publishers, Dordrecht, The Netherlands, 497 pp.

Tucker, A., 1972. The Toxic Metals. Earth Island Ltd., London, 237 pp.

Underwood, E.J., 1977. Trace Elements in Human and Animal Nutrition. Academic Press, New York.

U.S. Environmental Protection Agency, 1980. Ambient Water Quality Criteria for Antimony. EPA 440/5-80- 020. Prepared for the Office of Water Regulations and Standards, Criteria Division, Washington, DC.

U.S. Environmental Protection Agency, 2009. National Recommended Water Quality Criteria. Office of Water, Office of Science and Technology, Washington, DC, 21 pp.

Van der Leeden, F., Troise, F.L., and Todd, D.K., 1990. The Water Encyclopedia, 2nd ed. Lewis Publishers, Inc., Chelsea, MI.

Van der Perk, M., 2006. Soil and Water Contamination. Taylor & Francis, Oxford, UK.

Van Kirk, R.W., and Hill, S.L., 2006. Modeling Predicts Trout Population Response to Selenium Based on Individual-Level Toxicity. Unpublished report. Mathematics Department, Idaho State University, Pocatello, ID.

Vijver, M.G., Van Gestel, C.A.M., Lanno, R.P., Van Straalen, N.M., and Peijnenburg, W.J.G.M., 2004. Internal metal sequestration and its ecotoxicological relevance: a review. Environmental Science and Technology, vol. 38, pp. 4705–4712.

Wallwork-Barber, M.K., Kyall, K., and Ferenbaugh, R.W., 1985. Thallium movement in a simple aquatic ecosystem. Journal of Environmental Health, vol. A20, no. 6, pp. 689–700.

Wang, W.X., and Fisher, N.S., 1999a. Assimilation efficiencies of chemical contaminant in aquatic invertebrates: a synthesis. Environmental Toxicology and Chemistry, vol. 18, pp. 2034–2045.

Wang, W.X., and Fisher, N.S., 1999b. Effects of calcium and metabolic inhibitors on trace element uptake in two marine bivalves. Journal of Experimental Marine Biology and Ecology, vol. 236, pp. 149–164.

Watershed Investigations Section, 2005. Review of the Effects of Copper on Salmonids Olfaction. Watershed Investigations Section, Watershed Protection, Environmental Services Department, City of San Jose, CA.

Wekell, J.C., Shearer, K.D., and Houle, C.R., 1983. High zinc supplementation of rainbow trout diets. The Progressive Fish Culturalist, vol. 45, pp. 144–147.

Wekel, J.C., Shearer, K.D., and Gauglitz, E.J., Jr., 1986. Zinc supplementation of trout diets: tissue indicatros of body zinc status. The Progressive Fish Culturist, vol. 48, pp. 205–212.

Wentsel, R., McIntosh, A., and Atchison, G., 1977. Sublethal effects of heavy metal contaminated sediment on midge larvae (*Chirinimus tentans*). Hydrobiologia, vol. 56, pp. 153–156.

Weres, O., Jaouni, R.-R., and Taso, L., 1989. The distribution, speciation, and geochemical cycling of selenium in a sedimentary environment, Kesterson Reservoir, USA. Applied Geochemistry, vol. 4, no. 6, pp. 543–563.

Wilson, N.J., Crow, D., and Hunter, K., 2004. Antimony distribution and environmental mobility at an historic antimony smelter site, New Zealand. Environmental Pollution, vol. 129, no. 2, pp. 257–266.

Wong, P.T.S., Maguire, R.J., Chau, Y.K., and Kramar, O., 1984. Uptake and accumulation of inorganic tin by a freshwater alga, *Ankistrodesmus falcatus*. Canadian Journal of Fisheries and Aquatic Sciences, vol. 41, pp. 1570–1574.

Wood, C.M., McDonald, M.D., Walker, P., Grosell, M., Barimo, J.F., Playle, R.C., and Walsh, P.J., 2004. Bioavailability of silver and its relationship to ionoregulation and silver speciation across a range of salinities in the Gulf toadfish (*Opsanus beta*). Aquatic Toxicology, vol. 70, no. 2, 137–157.

Woodward, D.F., Goldstein, J.N., Farag, A.M., and Brumbaugh, W.G., 1997. Cutthroat trout avoidance of metals and conditions characteristic of a mining waste site: Coeur d'Alene River, Idaho. Transactions of the American Fisheries Society, vol. 126, pp. 699–706.

14
Biological Sampling and Inventory Process

JEFF SKOUSEN, CRAIG MAINS, AND JAMES A. JACOBS

One way to assess the health of the aquatic environment near potential or proven acid drainage areas is to evaluate the presence or absence and relative abundance of sensitive aquatic and plant species. The environment could include streams, rivers, lakes, floodplains, ponds, and bays adjacent to acid generation areas. Some of these environments might vary considerably as to species diversity and other important geochemical conditions, such as salinity, dissolved oxygen, temperature range and variation, rainfall, humidity, and other factors. Comparing the affected area to background abundance in nearby but unaffected areas can provide a biological assessment of the area affected.

Introduction

As part of a biological assessment, the U.S. Environmental Protection Agency (1995) estimated that about 6000 miles of streams are affected by acid mine drainage in the northern Appalachian area (Table 14.1), one of the most heavily affected areas in the United States. This high-sulfur coal area has regionwide problems of poor water quality, including low-pH water, high concentrations of dissolved metals, and distinct orange–yellow staining referred to as “yellow boy,” caused by the precipitation of iron hydroxide and other metals onto streambed rocks and sediment.

Table 14.1 Stream Miles Affected by Acid Mine Drainage in Five American States

State	Zero Fish	Some Fish	Total Miles
Pennsylvania	1714	1525	3239
West Virginia	488	612	1100
Ohio	258	349	607
Maryland	42	110	152
Virginia	17	0	17
Total	2519	110	152

Source: U.S. Enviornmental Protection Agency (1995).

Sampling for Benthic Macroinvertebrates

In addition to sampling for geochemical parameters such as pH, alkalinity, electrical conductivity, dissolved oxygen, oxidation–reduction potential, total dissolved solids, temperature, and turbidity, biological sampling and inventory processes are other ways to examine the health of a stream's ecosystem. One inexpensive way to assess stream health has been by using the *save our streams* (SOS) *method*. The SOS method was developed by the Izaak Walton League of America and the Ohio Department of Natural Resources. It uses benthic macroinvertebrates, which are aquatic organisms, to gauge stream quality. Benthic macroinvertebrates are aquatic organisms that live in the benthic environment, or stream bottom, are relatively large, and are invertebrates or organisms with no

backbones. Benthic macroinvertebrates (also called *benthos*) include not only numerous aquatic insects, but also organisms such as crayfish, scuds, worms, snails, and clams. The SOS method classifies the benthos according to their sensitivity to disruption from changing environmental conditions, primarily the introduction of contaminants. The SOS method can be used by stream restoration volunteers, but can also be upgraded by environmental professionals to be more rigorous in the field, if needed. By netting a representative sample of benthic organisms and checking on the organism's diversity and sensitivity to pH or metals exposure, the SOS method provides an approximation of stream health. Collecting benthos with a net in a shallow stream is shown in Figure 14.1.

FIGURE 14.1 Collecting a benthic sample using a net.

The higher the exposure of an organism to environmental stresses caused by elevated acidity or metals concentrations, the less likely the chances of observing robust individuals within a species, large population counts within a species, or a large variety of different species. Because benthos are relatively stationary in a short section of a stream and are exposed continuously to the full range of water quality conditions, they are representative of overall stream quality over a period of time, not just at the time the sample was collected. By contrast, fish are less representative of localized water quality because they can move upstream or into a side tributary to avoid poor water quality and return when conditions improve.

Key terms for biological sampling in acid drainage areas follow.

- *Benthic macroinvertebrates:* bottom-dwelling stream organisms that are large enough to be seen by the naked eye and that do not have backbones. They are mostly aquatic insects, but they also include worms and some crustaceans and mollusks.
- *Benthos:* a collection of organisms living on or in stream, river, sea, or lake bottoms.
- *Biodiversity:* refers to the number of different types of organisms; used as an indicator of stream quality.
- *Bioindicators:* living organisms that are used to gauge environmental quality based on their sensitivity or tolerance to contamination.
- *Habitat:* the place or type of site where an organism commonly lives. Organisms sometimes have very specific habitats. For example, some insects may be found only under rocks in riffles, whereas others will only be found burrowing in mud along banks.
- *Larva* (plural: *larvae:*) an immature form of an insect (some immature amphibians are also called larvae). It does not resemble the adult form and must undergo a distinct metamorphosis, changing into a pupa, from which the adult eventually emerges. Wings develop internally. Examples of aquatic insects that have a larval stage are caddisflies, dobsonflies, and craneflies.
- *Nymph:* an immature form of insect. It undergoes a less complicated metamorphosis than that of larvae and more closely resembles the adult insect. Wings develop externally. Examples are stoneflies, mayflies, and dragonflies.
- *Organism:* any living entity.

Benthos are preferred as bioindicators for several reasons:

- The organisms have known sensitivities or tolerances to contamination or changes in the environment.
- The presence or absence of different groups provides information on water quality.
- Benthos are easy to collect.
- Benthos can be collected using a handheld net called a kick seine.
- Benthos are easier to collect than fish, which are more mobile.
- Benthos are easy to identify without a microscope.

A hand lens is useful for benthos identification. Many of the benthos are the immature stages of flying insects, called *larvae* or *nymphs*. The aquatic stage typically lasts longer than the winged stage, often a year or more. A sample that includes a variety of sensitive organisms of different ages is an indication that the water quality has been good for a period of time, not just at the immediate moment. Measurement of benthics is sometimes more useful than taking a water sample, because these organisms have been exposed to a longer-term range of water quality conditions than has a one-time collection of a water sample and measurement of its chemistry. The water sample reports the chemistry at the exact moment the sample was taken, whereas the benthic sampling gives a measure of the overall conditions (sometimes the lowest threshold) of the water over time. Benthic monitoring is inexpensive since little equipment is needed.

Collecting a Benthic Sample

When possible, the sample is collected in a riffle section of the stream. A *riffle* is a section of the stream

that is usually shallow, with relatively rapidly moving water, a somewhat higher gradient, and mostly larger rocks. Ideally, it should have mostly cobble-size rocks. *Cobbles* are rocks that are 2 to 10 in. across. There may be a mixture of gravel and small, movable boulders on the streambed. Riffles are considered to be optimal habitats for many types of benthic organisms. The turbulence in riffle areas helps to keep the water well oxygenated. The current carries in organic matter that the benthos can use as food, and the void spaces between the rocks provide a refuge from the current and from predators. Benthic organisms are not evenly distributed on the stream bottom. Although there are benthos in the pools, generally there are higher numbers and a greater variety of benthos species in riffle areas. In some streams it may be difficult or impossible to find a good riffle. In these cases, alternative sampling methods may be used. But when sampling is possible in cobble riffles, results between samples taken in different sections of the streams and between different streams can be compared.

SOS Method

The SOS method is inexpensive and practical. It requires that three separate subsamples of 1 square yard each be collected. Once collected, the benthos can be separated and identified at the stream side. Some monitors prefer to preserve the samples in alcohol and identify them later. It may be necessary to get permission from a state agency to preserve and remove benthos rather than returning them live to the stream.

Rating Stream Quality

The SOS method divides the benthos into 24 biological groups or taxa (see the section “Sample Collection Exercise and Evaluation” for an example of the biological inventory paperwork). These taxa are combined into three larger groups based on their general sensitivity to contamination as shown on the two pages labeled “Stream Insects and Crustaceans.” Sorting and identifying the benthos in the field are shown in Figure 14.2.

FIGURE 14.2 Sorting and identifying the benthos in the field.

The first group consists of organisms that are generally considered to be sensitive to contamination. They are typically found in clean, unpolluted streams. The second group consists of organisms that are considered to be somewhat less sensitive to contamination and are found in a wider range of stream conditions. The third group is considered to be contamination tolerant. They may be present in clean streams, but in some cases they may be the only organisms present in polluted streams, as the more sensitive organisms are eliminated. Once the benthos have been sorted and identified, the stream rating can be calculated. The SOS method uses a weighted system to obtain a numerical value. An example data sheet to show the rating system appears at the end of this section. Each taxon present in the sensitive group is worth 3 points. Although the relative abundance of each taxon is worth recording, the number of organisms in each taxon is not considered for the calculation—just their presence or absence. Each taxon present in the somewhat-sensitive group is worth 2 points each, and each taxon present in the contamination-tolerant group is worth 1 point. On the example data sheet for the example run site, three taxa were present from the sensitive group, worth 3 points each, for a total of 9 points; four taxa were present in the somewhat-sensitive group, worth 2 points each, for 8 points; and two taxa were present from the tolerant group, worth 1 point each, for 2 points. The total number for this sample was 19 points, which places it in the good range. The SOS method requires that three separate subsamples be collected. In the example there was a slightly different mix of organisms present in the other two subsamples: The second was worth 21 points and the third was worth 18 points. We take the highest of the three subsamples, which was the second. The 21 points falls into the good range. An example problem is

included to provide an opportunity to practice calculating the water quality rating.

Using the SOS Method in Acid Mine Drainage–Affected Streams

Rating water quality using benthos is not an exact science, especially when using a simplified method. The results do not always match a visual, preconceived estimation of stream quality. For example, small headwater streams that might be considered pristine often are naturally low in nutrients and as a result may be low in both diversity and abundance of benthos. Typically, as streams get larger, more nutrients are available and the potential for higher numbers and diversity of organisms increases. Sometimes the nutrients may be present due to the discharge of household wastewater from faulty septic systems or as waste runoff from farm animals. It may be difficult to think of these sources, which are generally thought of as pollutants, as causing an increase in water quality ratings for benthos. However, as long as the input of these nutrient-laden materials is small, this may sometimes be the case. But when the flow of nutrients becomes excessive, diversity and water quality ratings decline, although the abundance of organisms may remain high. In other words, there may be only a few types of organisms, but there are usually a lot of them.

In some ways, using the SOS method to monitor the effects of acid mine drainage is clearer. Unlike nutrient contamination, where a small amount can actually stimulate aquatic life, acid mine drainge has a direct toxic effect. Acid mine drainage eliminates aquatic life in at least three ways. The acidic conditions alone eliminate many aquatic organisms. The dissolved metals are also toxic to many organisms, and when the metals settle out on the stream bottom as an insoluble deposit, they fill the spaces between rocks, thereby eliminating the habitat for benthos. Any one of these can result in a decrease in aquatic life, but together, the effect can be dramatic. In some streams where acid mine drainage contamination is severe, it may be difficult to find any benthic life at all. The effect of dilution is also typically proportional. A small discharge of acid mine drainage into a large stream may not have a noticeable effect. A noticeable decrease in numbers and diversity of organisms will be detected as the proportion of acid mine drainage increases relative to the flow of the stream it is entering. It is still common to find the discharge from a single abandoned mine entering a healthy stream and almost completely eliminating all benthic life downstream.

In general, because the benthos react to acid mine drainage in an obvious way, the SOS method makes a good monitoring tool for watershed groups working in acid mine drainage–affected watersheds. There is usually a clear-cut difference between stream segments that are affected heavily, affected moderately, or are undisturbed. This makes the method useful for groups trying to document the impact of acid mine drainage in different parts of the watershed and also to document the recovery of aquatic life after reclamation and water remediation projects. It is worthwhile to be aware that benthic organisms do not necessarily respond to different types of contaminants in the same way, and some organisms that may be tolerant to organic contamination may be sensitive to acid mine drainage. Some types of midge larvae can sometimes be found even in very strong acid mine drainage. The composition of benthic life in a stream that receives alkaline mine drainage or treated acid mine drainage may also differ from that of an undisturbed stream.

Sample Collection Exercise and Evaluation

We illustrate the technique for sample collection and evaluation with the following example.

SAMPLING A RIFFLE FOR MACROINVERTEBRATES

Step 1 - Locate a Sampling Site - Site should have easy public access (if it's on private property ask for permission from the land owner, if denied find another site) and be strategically located in the watershed. The site should be a riffle large enough to take 3 samples with at least 60% Cobble (stones 2 to 10 inches in diameter). This isn't always possible especially in heavily silted streams but this can be indicated on the Stream Quality Survey (SQS).

Step 2 - Placing the Net - Approach the sample site from downstream taking care not to disturb the sample area. The net holder should position the net directly across the current and hold it at a 45 degree angle but water should not be able to pass over the net. The sampler anchors the bottom of the net with rocks. The sampler determines a 3' x 3' area in front of the net as the sample area.

Step 3 - Rock Rub - The sampler(s) takes the larger rocks, starting at the back of the sampling area, and rubs them throughly in front of the net. This dislodges any invertebrates clinging to the rock and the current sweeps them into the net. After rubbing the rocks set them outside the sampling area. An optional technique is to use a 5 gallon white bucket with several inches of water to store the large rocks for rubbing later. Rub the rocks in the water in the bucket checking them to make sure all organisms have been dislodged before returning the rocks to the stream. This technique is especially helpful during low water conditions because it reduces the loss of organisms due to weak currents. A bucket is also helpful when there is a large amount of leaf or stick litter in the net.

Step 4 - The Dance - The sampler(s) start at the back of the sample area again, they pivot their feet until they stir up several inches of the substrate. Continuing to stir up the substrate they proceed from the back of the sampling area towards the front until they reach the net.

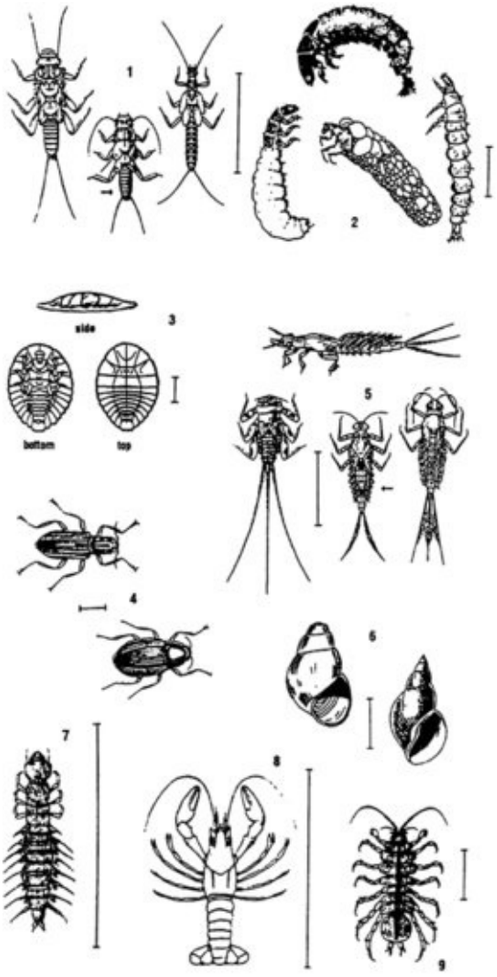
Step 5 - Lift the Net - Remove the rocks anchoring the bottom of the net and rub them in front of the net. The net holder lifts the poles and the sampler lifts the bottom of the net in the middle. When lifting bring the net forward and then lift. This will "scoop" the organisms into the middle of the net.

Step 6 - Picking the Net - Spread the net on a white or light colored piece of plastic such as a white garbage bag. Pick the invertebrates from the net and place them in a white pan with a couple inches of water in it. For small invertebrates a white ice cube tray filled with creek water is handy for seperating and counting different types. If using a bucket for the rock rub pour the contents into a white pan, let the sediment settle until all organisms can be seen, identified and counted.

Step 7 - Count and Record - Carefully identify the captured organisms. Record their numbers, or relative numbers using A for 1 to 9, B for 10 to 99 and C for more than 100, on the sampling worksheet for Sample #1. Record the next two samples on the worksheet also. Take the sample with the highest score and record those results on the Stream Quality Survey. Remember to record the habitat assessments and land uses on the Stream Quality Survey also.

Equipment:

Kick seine net
White shallow pan and/or white ice cube trays
Macroinvertebrate identification card, sampling worksheets and surveys
Thermometer
Magnifying glass or magnicubes
Plastic trash bag or other plastic tarp to place under the net
Tweezers (optional)
pH or other test kits (optional)
Clipboard (optional), pen or pencil
Gloves
5 gallon bucket (optional)
Spray bottle (optional)



Bar lines indicate relative size

1/95

Stream Insects & Crustaceans

GROUP ONE TAXA

Pollution sensitive organisms found in good quality water.

1 ***Stonefly: Order Plecoptera.*** 1/2" - 1 1/2", 6 legs with hooked tips, antennae, 2 hair-like tails. Smooth (no gills) on lower half of body. (See arrow.)

2 ***Caddisfly: Order Trichoptera.*** Up to 1", 6 hooked legs on upper third of body, 2 hooks at back end. May be in a stick, rock or leaf case with its head sticking out. May have fluffy gill tufts on underside.

3 ***Water Penny: Order Coleoptera.*** 1/4", flat saucer-shaped body with a raised bump on one side and 6 tiny legs and fluffy gills on the other side. Immature beetle.

4 ***Riffle Beetle: Order Coleoptera.*** 1/4", oval body covered with tiny hairs, 6 legs, antennae. Walks slowly underwater. Does not swim on surface.

5 ***Mayfly: Order Ephemeroptera.*** 1/4" - 1", brown, moving, plate-like or feathery gills on sides of lower body (see arrow), 6 large hooked legs, antennae, 2 or 3 long, hair-like tails. Tails may be webbed together.

6 ***Gilled Snail: Class Gastropoda.*** Shell opening covered by thin plate called operculum. When opening is facing you, shell usually opens on right.

7 ***Dobsonfly (Hellgrammite): Family Corydalidae.*** 3/4" - 4", dark-colored, 6 legs, large pinching jaws, eight pairs feelers on lower half of body with paired cotton-like gill tufts along underside, short antennae, 2 tails and 2 pairs of hooks at back end.

GROUP TWO TAXA

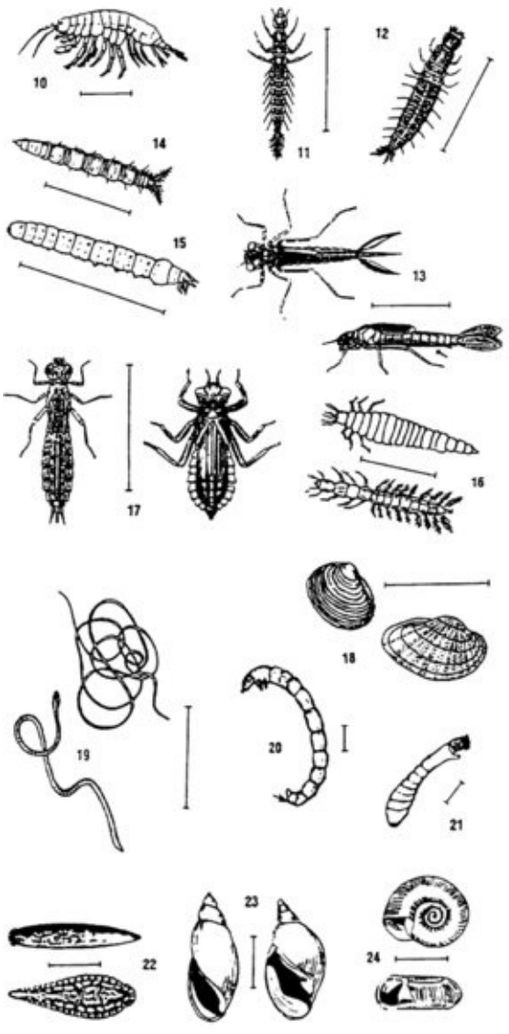
Somewhat pollution tolerant organisms can be in good or fair quality water.

8 ***Crayfish: Order Decapoda.*** Up to 6", 2 large claws, 8 legs, resembles small lobster.

9 ***Sowbug: Order Isopoda.*** 1/4" - 3/4", gray oblong body wider than it is high, more than 6 legs, long antennae.

Save Our Streams

Izaak Walton League of America
707 Conservation Lane
Gaithersburg, MD 20878-2983
1(800)BUG-IWLA



Bar lines indicate relative size

GROUP TWO TAXA CONTINUED

10 ***Scud: Order Amphipoda.*** 1/4", white to grey, body higher than it is wide, swims sideways, more than 6 legs, resembles small shrimp.

11 ***Alderfly Larva: Family Sialidae.*** 1" long. Looks like small hellgrammite but has 1 long, thin, branched tail at back end (no hooks). No gill tufts underneath.

12 ***Fishfly Larva: Family Corydalidae.*** Up to 1 1/2" long. Looks like small hellgrammite but often a lighter reddish-tan color, or with yellowish streaks. No gill tufts underneath.

13 ***Damselfly: Suborder Zygoptera.*** 1/2" - 1", large eyes, 6 thin hooked legs, 3 broad oar-shaped tails, positioned like a tripod. Smooth (no gills) on sides of lower half of body. (See arrow.)

14 ***Watersnipe Fly Larva: Family Athericidae (Atherix).*** 1/4" - 1", pale to green, tapered body, many caterpillar-like legs, conical head, feathery "horns" at back end.

15 ***Crane Fly: Suborder Nematocera.*** 1/3" - 2", milky, green, or light brown, plump caterpillar-like segmented body, 4 finger-like lobes at back end.

16 ***Beetle Larva: Order Coleoptera.*** 1/4" - 1", light-colored, 6 legs on upper half of body, feelers, antennae.

17 ***Dragon Fly: Suborder Anisoptera.*** 1/2" - 2", large eyes, 6 hooked legs. Wide oval to round abdomen.

18 ***Clam: Class Bivalvia.***

GROUP THREE TAXA

Pollution tolerant organisms can be in any quality of water.

19 ***Aquatic Worm: Class Oligochaeta.*** 1/4" - 2", can be very tiny, thin worm-like body.

20 ***Midge Fly Larva: Suborder Nematocera.*** Up to 1/4", dark head, worm-like segmented body, 2 tiny legs on each side.

21 ***Blackfly Larva: Family Simuliidae.*** Up 1/4", one end of body wider. Black head, suction pad on other end.

22 ***Leech: Order Hirudinea.*** 1/4" - 2", brown, slimy body, ends with suction pads.

23 ***Pouch Snail and Pond Snails: Class Gastropoda.*** No operculum. Breathe air. When opening is facing you, shell usually opens on left.

24 ***Other Snails: Class Gastropoda.*** No operculum. Breathe air. Snail shell coils in one plane.

04.22.2010 08:58

04.22.2010 09:01

DOWNSTREAM ALLIANCE
STREAM MONITORING FIELD SHEET

9-25-99 Stream: EXAMPLE RUN Location ID#: 3-9

Tributary to: BIG SANDY CREEK

Location on stream: ABOUT 30 YDS. ABOVE COUNTY ROAD 14/8

USGS topo quad: VALLEY POINT Lat. 39° 36' 56" Long. 79° 43' 10"

Substrate description (silt, gravel, cobbles, etc.) RIFFLE APPROX. 60% COBBLES, 20% SMALL BOULDERS, 20% GRAVEL.

Water temp. 60°F conductivity: 70 µS

70 pH method: HACH WR other tests:

Observations: STREAM LOOKS GOOD IN THIS STRETCH. NO SIGNS OF EROSION, NO DISCOLORATION OF STREAMBED DEPOSITS.

Benthic samples collected by: CM, CW

Sensitive		Somewhat-sensitive		Tolerant	
33	caddisfly larvae		beetle larvae	2	aquatic worms
	hellgrammites		clams		blackfly larvae
53	mayfly nymphs	2	cranefly larvae		leeches
	gilled snails	1	crayfish	11	midge larvae
	riffle beetles		damselfly nymphs		pouch/pond snails
21	stonefly nymphs	1	dragonfly nymphs		other snails
	water penny larvae	13	scuds		
			sowbugs		
			fishfly larvae		
			alderfly larvae		
			snipefly larvae		
3 # of taxa present x 3 =		4 # of taxa present x 2 =		2 # of taxa present x 1=	
9 index value +		8 index value +		2 index value=	

Now add together the three index values = 19 total index value.

Sensitive		Somewhat-sensitive		Tolerant	
89	caddisfly larvae		beetle larvae	3	aquatic worms
	hellgrammites		clams		blackfly larvae
67	mayfly nymphs	4	cranefly larvae		leeches
	gilled snails	2	crayfish	14	midge larvae
	riffle beetles		damselfly nymphs		pouch/pond snails
24	stonefly nymphs		dragonfly nymphs		other snails
	water pennies	23	scuds		
			sowbugs		
		2	fishfly larvae		
		1	alderfly larvae		
			snipefly larvae		

3 # of taxa present x 3 = 9 index value +

5 # of taxa present x 2 = 10 index value +

2 # of taxa present x 1 = 2 index value =

Add together the index values = 21 total index value.

Sensitive		Somewhat-sensitive		Tolerant	
46	caddisfly larvae		beetle larvae		aquatic worms
	hellgrammites		clams		blackfly larvae
48	mayfly nymphs	1	cranefly larvae		leeches
	gilled snails	4	crayfish	8	midge larvae
	riffle beetles		damselfly nymphs		pouch/pond snails
18	stonefly nymphs		dragonfly nymphs		other snails
	water pennies	16	scuds		
			sowbugs		
		4	fishfly larvae		
			alderfly larvae		
			snipefly larvae		

3 # of taxa present x 3 = 9 index value +

4 # of taxa present x 2 = 8 index value +

1 # of taxa present x 1 = 1 index value =

Add together the three index values = 18 total index value.

WATER QUALITY RATING - based on highest of total index values

☐	Very good (>22)	☑	Good (17-22)
☐	Fair (11-16)	☐	Poor (< 11)

9-21-18

DOWNSTREAM ALLIANCE
STREAM MONITORING FIELD SHEET

Date: _____ Stream: _____ Location ID#: _____

Tributary to: _____

Location on stream: _____

USGS topo quad: _____ Lat. _____ Long. _____

Substrate description (silt, gravel, cobbles, etc.): _____

Water temp. _____ conductivity: _____

pH: _____ pH method: _____ other tests: _____

Observations: _____

Benthic samples collected by: _____

Sensitive	Somewhat-sensitive	Tolerant
☐ caddisfly larvae	☐ beetle larvae	☐ aquatic worms
☐ hellgramunites	☐ clams	☐ blackfly larvae
☐ mayfly nymphs	☐ cranefly larvae	☐ leeches
☐ gilled snails	☐ crayfish	☐ midge larvae
☐ riffle beetles	☐ damselfly nymphs	☐ pouch/pond snails
☐ stonefly nymphs	☐ dragonfly nymphs	☐ other snails
☐ water penny larvae	☐ scuds	
	☐ sowbugs	
	☐ fishfly larvae	
	☐ alderfly larvae	
	☐ snipefly larvae	
☐ # of taxa present x 3 =	☐ # of taxa present x 2 =	☐ # of taxa present x 1=
index value +	index value +	index value=

Now add together the three index values = total index value.

The blank field sheet is used to calculate water quality ratings.

- *First subsample:* In this sampling, the following numbers of organisms were netted: caddisfly larvae (13); cranefly larvae (3); crayfish (1); worms (5); midge larvae (11).
- *Second subsample:* In this sampling, the following numbers of organisms were netted: caddisfly larvae (10); cranefly larvae (2); crayfish (1); fishfly larvae (2) worms (7); midge larvae (12).
- *Third subsample:* In this sampling, the following numbers of organisms were netted: caddisfly larvae (8); crayfish (1); dragonfly nymphs (1); worms (2); midge larvae (10); blackfly larvae (1).

Data Evaluation

The first subsample is worth 9 points total. One sensitive taxon (caddisflies) was present, for a subtotal of 3 points. Two somewhat-sensitive taxa were present (craneflies and crayfish) for 2 points each, for a subtotal of 4 points. Two tolerant taxa were present (worms and midges) for 1 point each, for a subtotal of 2 points.

The second subsample is worth 11 points total. One sensitive taxon (caddisflies) was present, for a subtotal of 3 points. Three somewhat-sensitive taxa were present (craneflies, crayfish, and fishflies) for 2 points each, for a subtotal of 6 points. Two tolerant taxa were present (worms and midges) for 1 point each, for a subtotal of 2 points.

The third subsample is worth 10 points total. One sensitive taxon (caddisflies) was present, for a subtotal

of 3 points. Three somewhat-sensitive taxa were present (crayfish and dragonflies) for 2 points each, for a subtotal of 4 points. Three tolerant taxa were present (worms, midges, and blackfly) for 1 point each, for a subtotal of 3 points.

Interpretation of the Data

The second subsample has the highest number of points, and the 11 points places this site in the fair range. Notice that the sample rates as fair based on the highest subsample rather than on an average of all three subsamples. Notice also that the number of organisms in each taxon did not affect the final rating, only the number of taxa.

Problems and Questions

1. Based on the sample exercise, leeches, aquatic worms, and blackfly larvae belong to which sensitivity category?
2. Explain why benthic organisms may be more indicative than fish of long-term site conditions in a stream or creek.
3. How might changes in the season affect counts of benthic microinvertibrates? Discuss possible changes in seasonal temperature, water flow, and sunlight.
4. How could one verify that decreases in the numbers of species reflects acid mine drainage as a cause, versus random or normal changes in species populations over time?
5. Why are stream riffles considered optimal habitats for many types of benthic organisms?

References and Suggested Reading

Hart, C.W., and Fuller S.L.H., eds., 1974. Contamination Ecology of Freshwater Invertebrates. Academic Press, New York, 389 pp. Covers the responses of all types of aquatic life to various pollutants (organic enrichment, toxic substances, acids, etc.).

Hynes, H.B.N., 1963. The Biology of Contaminated Waters. Liverpool University Press, Liverpool, UK, 202 pp. A scientific but readable account of the effects of contamination on aquatic life.

Izaak Walton League of America, 2010. Save Our Streams (SOS) protocol. http://www.iwla.org/index.php?ht=d/sp/i/1977/pid/1977.

Lemkuhl, D., 1979. How to Know the Aquatic Insects. Pictured Key Nature Series. Wm. C. Brown, Dubuque, IA, 168 pp. Illustrated keys to the family level. Has some information on contamination and aquatic insects as indicators.

McCafferty, W.P., 1981. Aquatic Entomology: The Fishermen's and Ecologists' Illustrated Guide to Insects and Their Relatives. Science Books International, Boston. Illustrated keys to the family level. Excellent illustrations, including 15 color plates.

Merritt, R.W., and Cummins K.W., eds., 1978. An Introduction to the Aquatic Insects of North America. Kendall/Hunt, Dubuque, IA, 441 pp. A standard source. Well-illustrated keys to family and genus. Information on ecology and habitats.

Plafkin, J.L., Barbour, M.T., Porter, K.D., Gross, S.K., and Hughs, R.M., 1989. Rapid Bioassessment Protocols for Use in Streams and Rivers: Benthic Macroinvertebrates and Fish. EPA/444/4-89-001. U.S. EPA, Office of Water, Washington, DC, 174 pp. Presents a series of bioassessment methods of increasing sophistication. Written for professionals but could be useful for motivated volunteers.

Skousen, J., and Mains, C., 1997. Watershed Characterization Handbook for Streams Impacted by Acid Mine Drainage: You Can't Judge a Stream by Its Color. West Virginia University, Extension Service, Morgantown, WV, 37 pp.

Terrel, C.R., and Perfetti, P.B., 1989. Water Quality Indicators Guide: Surface Water. SCS-TP-161. U.S. Soil Conservation Service, Washington, DC, 128 pp. Focuses on agricultural water quality problems but has good readable information on aquatic life as indicators, including algae, benthos, plants, and fish.

U.S. Environmental Protection Agency, 1995. Streams with Fisheries Impacted by Acid Mine Drainage in MD, OH, PA, VA and WV. Published map and report. U.S. EPA, Region 3, Wheeling, WV.

U.S. Environmental Protection Agency, 1997. Volunteer Stream Monitoring: A Methods Manual. EPA 841-B-97-003. U.S. EPA, Office of Water, Washington, DC, 210 pp.

U.S. Environmental Protection Agency, 2010a. Superfund Risk Assessment: Risk Management. On-Line Technical Paper. http://www.epa.gov/oswer/riskassessment/superfund_management.htm.

U.S. Environmental Protection Agency, 2010b. Overview of Ecological Risk Assessment Analysis Phase: Exposure Characterization. On-Line Technical Paper. http://www.epa.gov/oppefed1/ecorisk_ders/toera_analysis_exp.htm.

U.S. Forest Service, 2010. Stream Notes. Stream Systems Technology Center. http://stream.fs.fed.us/news/streamnt/jul02/jul_02_05.htm.

15
Acid Rock Drainage as Related to Permafrost, Glaciers, And Climate Change

BRUCE W. DOWNING AND JAMES A. JACOBS

The effects of climate change are showing up in a variety of worldwide environments, resulting in a potential for more pyrite oxidation. Changes in the location of glacier ice can greatly affect acid rock drainage in areas where glaciers have scoured pyrite-rich rocks and the glacier ice has been providing a cover to prevent oxidation of the iron sulfides.

Introduction

With global climate changes occurring, many mountain glaciers in areas with unmined ore bodies on the surface have been retreating, exposing new surfaces of iron sulfide rocks to the atmosphere, creating acid rock drainage (ARD). Even in coastal areas where acid sulfate soils are present, increases or decreases in water elevation affect pyrite oxidation and the associated production of sulfuric acid and trace metal concentrations. Rising sea levels and the frequency of extremely high seas from storm surges have had a significant effect on coastlines. All of these predicted climate change effects have direct relevance for countries with coastal acid sulfate soils. Sulfide oxidation may increase with drought and the exposure of pyrite-rich rocks to the atmosphere. In other cases, rising sea levels or flooding of coastal acid sulfate soils lowers acid drainage and associated metal concentrations by recreating reducing conditions, putting a stop to the oxidation of iron sulfide minerals.

Acid Rock Drainage and Permafrost

Acid rock drainage has become a major topic with respect to mining and the environment in permafrost regions, most notably Canada and Alaska. Similar issues are likely to occur in northern Russia and the Scandinavian countries as well. Permafrost is defined when the layers of soil exist continuously at a temperature below freezing.

Specialized microbes exist in the permafrost. Microbial activity increases with rises in temperature. In areas where permafrost ice melts, surface water with dissolved oxygen levels up to 8 mg/L will percolate into the formerly frozen soil matrix, leading to microbial-enhanced oxidation of those materials. The oxidation of pyrite-rich soils can create acid drainage.

The issue of acid drainage has become important in the recent mine development review of potential diamond mines in northern Canada and gold mines in central Alaska. Natural acid rock generation and drainage processes, resulting in natural gossan development, is very slow in permafrost areas. Microbial activity is also limited under freezing conditions. Some rocks, such as kimberlites, may be quite permeable, and hence water movement will occur through these bodies, even though they may occur within permafrost areas. Studies of ARD and its impact on the permafrost environment have become quite numerous in the past five years.

Several websites have information on permafrost:

- Geological Survey of Canada: sts.gsc.nrcan.gc.ca/ permafrost
- International Permafrost Association: www.geodata.soton.ac.uk/ipa/f_main.html
- U.S. Department of Agriculture: http://efotg.sc.egov.usda.gov/references/public/ak/permafrost8_02.pdf
- National Snow and Ice Data Center: http://nsidc.org/data/docs/fgdc/ggd318_map_circumarctic/index.html

Water Flow in Permafrost

There is a widespread assumption that permafrost is frozen so that essentially there is no groundwater movement. The question of discontinuous and continuous permafrost is important, as this will allow groundwater flow. There are active layers within the permafrost, specifically near the surface, as well as scattered areas of taliks, which are essentially areas of unfrozen ground near the surface which are conduits for groundwater movement. Permafrost will be disturbed during construction activities and the dumping of waste rock, which has the potential to break down the permafrost at and near the surface. If a developer builds a protective layer on top of the permafrost so as to keep this material frozen, surface water percolating through the waste dump must flow somewhere and be collected during mining operations. If the layer is not frozen continuously, this water will percolate into the ground and flow as groundwater (which will need to be monitored for contamination).

ARD Prediction and Permafrost

The aspect of ARD prediction in permafrost will depend on local climatic conditions for long-term mitigation and engineering; however, the tools for ARD prediction are similar for nonpermafrost areas. The long-term effects that should be determined include global warming, which may aid in the destruction of permafrost, and water treatment may become a more important issue at that time. The use of field test pads for ARD prediction is definitely warranted in conjunction with laboratory test work. The duplication of field conditions in the laboratory for kinetic and column leach tests is not really possible---thus the need for field test areas.

Recent kimberlite discoveries in northern Canada have had an impact on our understanding of ARD in areas of permafrost, especially for mine permitting and ultimate water quality studies. The onset of ARD in these areas is relatively slow at present, and natural ARD sites are not common. There are very few published cases studies dealing with ARD in permafrost areas.

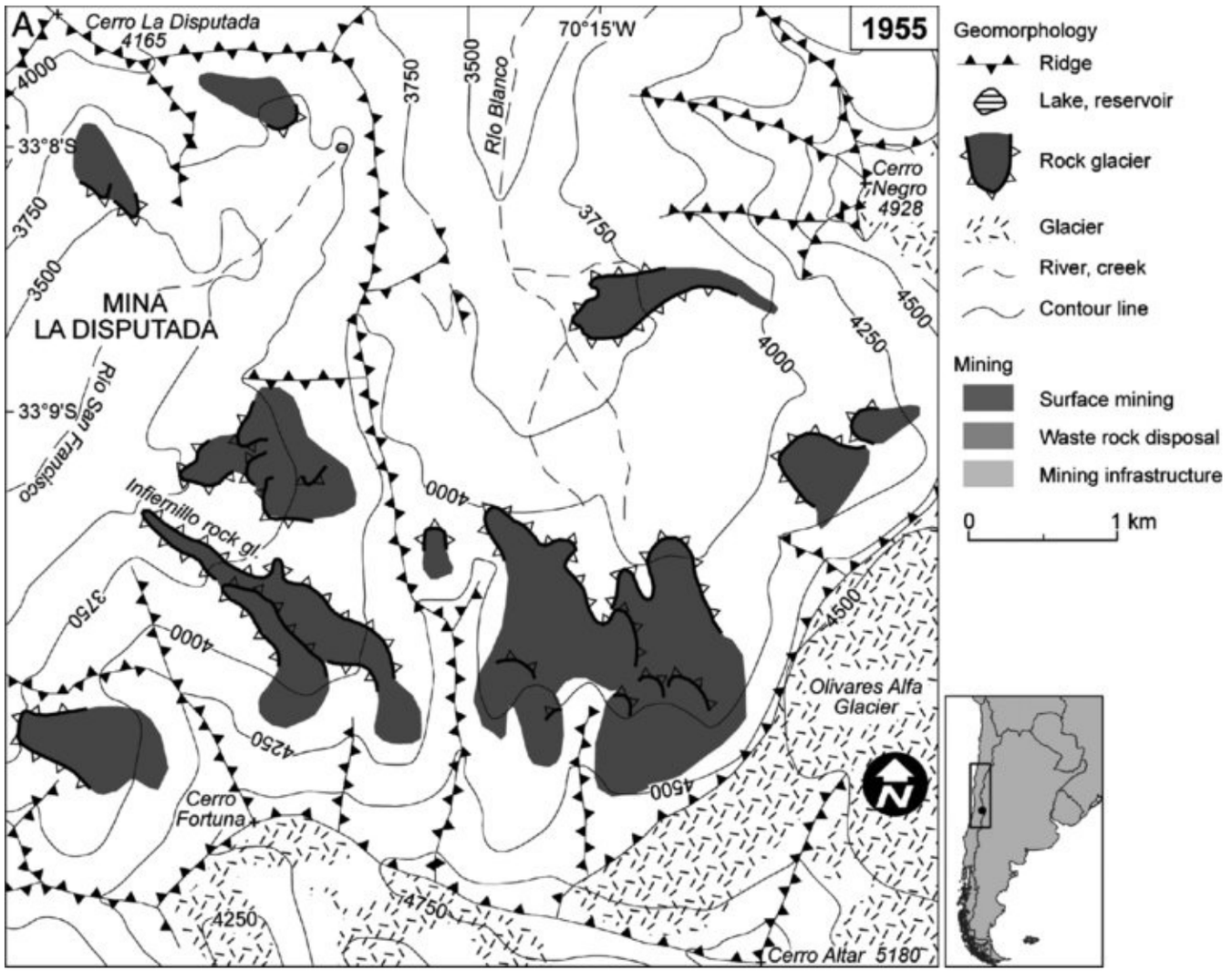
Acid Rock Drainage and Retreating Glaciers

Glaciers and rock glaciers in the semiarid Andes provide natural stores of water that control the runoff of mountain rivers, especially during the dry summer months. Rock glaciers are a minor hydrological and geomorphological importance in the Alps of Europe, however, the amount of water stored per unit area in the Chilean Andes between Santiago and Mendoza, Chile is one magnitude higher than that in the Alps (Brenning, 2008).

Acid rock drainage is associated with retreating glaciers in several ways:

1. Retreating glaciers may expose previously covered rocks containing elevated concentrations of pyrite or other sulfides, which have the potential to generate and release acid and dissolved metals where the glaciers once existed.

2. As alpine glaciers are retreating in many parts of the world, not only are water supplies being threatened, but mud slides and debris flows are becoming more common in these mountain areas. Sometimes, as in Chile, these mountain areas also contain sulfur-rich metal ores. Increased mining activity near retreating glaciers has been well documented (Brenning, 2008). Locations of mining wastes and rock glaciers in an area in Chile are shown in Figure 15.1.



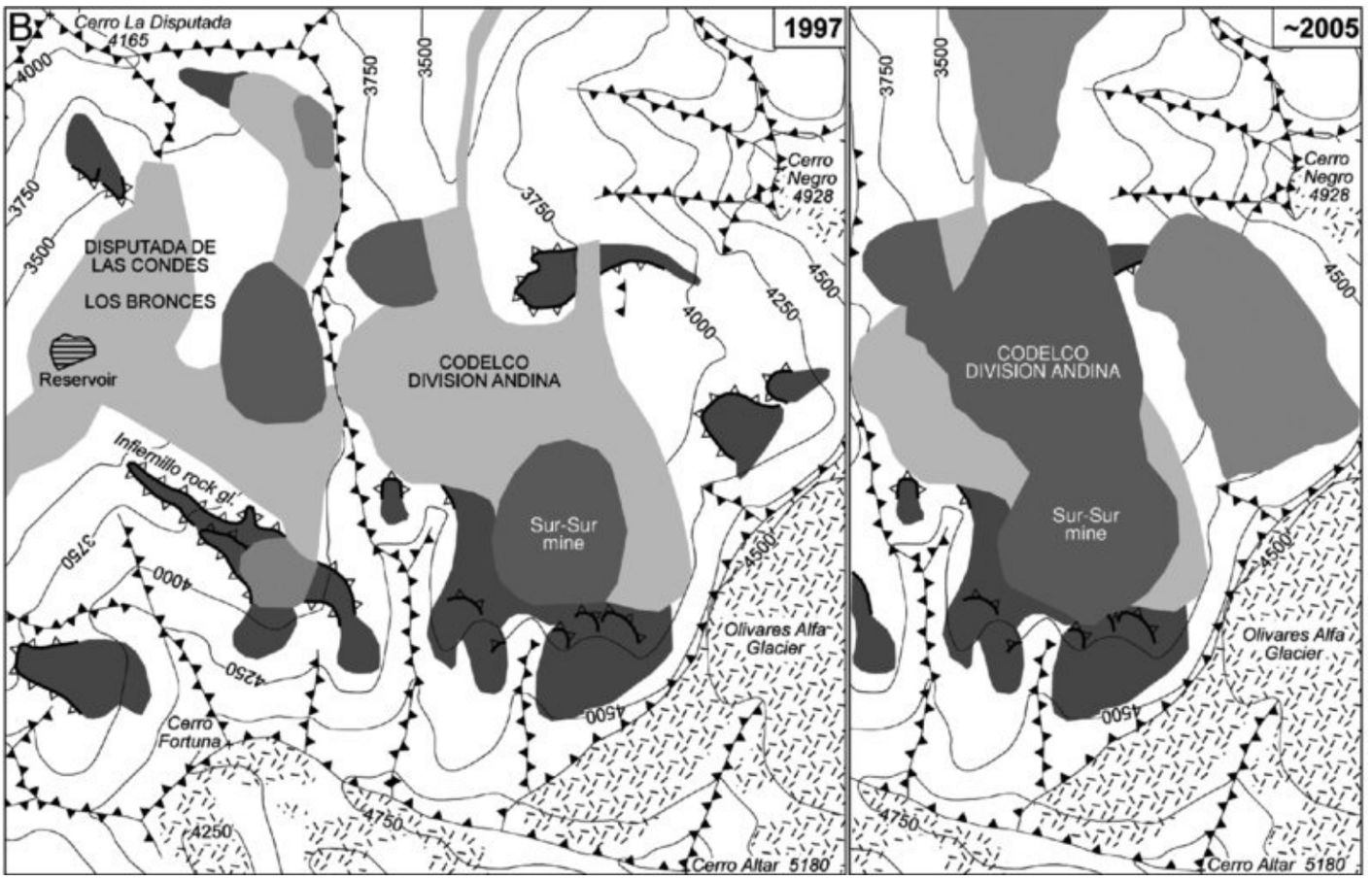


FIGURE 15.1 Geomorphological impact of open-pit mining on rock glaciers at División Andina and Los Bronces: (A) 1955; (B) 1987 and 2005. Cartography based on Llibountry (1961), Arcadis Geotécnica (2001), and aerial photography of 1955 and 1997 (Hycon, No. 4300, and Geotec, flight Juncal, No. 5585).

Increased water flow from retreating glaciers onto nearby sulfur-rich mining waste rock may produce acid rock drainage. The geochemical weathering of the mining waste rock piles may produce acid rock drainage, affecting downstream water discharge, even after mine closure (Ripley et al., 1995; Andía et al., 1999; U.S. Environment Protection Agency, 2001).

Debris flows and mud slides can also erode or disturb topographically lower mining waste rock piles, exposing sulfur-rich rocks to increased oxidation. Debris flows or mud slides can also be deposited so that they divert water flow paths, creating erosion and instabilities in nearby mining waste rock piles. Chilean researchers have found that more than half of the 120 glaciers they monitor are shrinking, with many disappearing at twice the rate recorded just a decade ago (Brenning, 2008). With the increased glacial meltwater flows and associated mountain instabilities in these mining areas, oxidation of freshly exposed pyrite-rich rocks is likely to become more widespread.

Acid Rock Drainage and Climate Change

Climate changes provide major shifts in rainfall, and the rising or lowering of surface water or groundwater levels has affected acid rock drainage generation. Rainfall events cause both increases and decreases in acid generation and trace metal concentrations and their loadings from mine wastes and unmined mineralized areas into receiving streams based on a study by the U.S. Geological Survey (Nordstrom, 2009). The study included data from three mines sites in the United States and other sites

elsewhere. Gradual increases in acid and metals concentrations occur during long dry spells, and sudden large increases are observed during the rising limb of the discharge following dry spells (first flush). By the time the discharge peak has occurred, metals concentrations have usually decreased, often to levels below those of prestorm conditions, and they rise slowly during the next dry spell. These dynamic changes in metals concentrations and loadings are related to the dissolution of soluble salts and the flushing out of waters that were concentrated by evaporation. The underlying processes, pyrite oxidation and host rock dissolution, do not end until the pyrite is fully weathered, which can take hundreds to thousands of years (Nordstrom, 2009).

These observations can be generalized to predict future conditions caused by droughts related to El Niño and climate change associated with global warming. Already, the time period for dry summers is lengthening in the western United States, and rainstorms are farther apart and more intense when they happen (Nordstrom, 2009). Consequently, due to the significant changes in rainfall, temperature, storm size and duration, and other climate fluctuations, storm water flushing of inactive and orphan mine sites, active mine sites, and mineralized but unmined sites will cause sudden larger increases in the generation of sulfuric acid and metals concentrations that will be an ever-increasing danger to aquatic life in nearby surface waters. Higher average concentrations will be observed during longer low-flow periods. As major changes in rainfall and temperature occur on a worldwide basis, the acid drainage mitigation efforts will have to increase the capacity of engineered designs to address the more extreme conditions, not average conditions of previous years.

Acid Sulfate Soils and Climate Change

While no warming occurred on our planet between 1998 and 2013, were we to again experience warming as some believe may occur, a variety of changes in sea level and storm patterns might be experienced. These changes could affect countries with coastal acid sulfate soils and have direct relevance for countries with coastal acid sulfate soils, either through exacerbating sulfide oxidation by drought and through exposing the soil to aerobic processes by a lowering of surface waters or groundwater. Rising sea or groundwater levels may have the tendency to restore reducing and anaerobic biogeochemical processes by flooding acid sulfate soils. The interaction of specific land management factors such as human-made drainage will also have a significant role in how the impacts of climate change that are predicted will affect these landscapes (Bush et al., 2010).

Understanding the potential impacts of climate change for coastal lowland acid sulfate soils is particularly important given the utility of these areas for potential agriculture and urban use. Since disturbing and aerating acid sulfate soils can cause extreme environmental degradation by generating sulfuric acid and releasing trace metals, it is apparent that these coastal areas are highly sensitive to climatic factors such as temperature and hydrology and susceptibility to sea-level inundation.

References and Suggested Reading

Andía, M.E., Lagos, G.E., and Danielson, L.J., 1999. The challenges posed by mine closure in Chile. In: Proceedings of the Copper ’99 International Conference, October 10–13, Phoenix, A. Minerals, Metals, and Materials Society, Warrendale, PA.

Arcadis Geotécnica, 2001. Estudio de Impacto Ambiental Proyecto de Expansión División Andina, Santiago, Chili.

Brenning, A., 2008. The impact of mining on rock glaciers and glaciers; examples from central Chile. In: Darkening Peaks: Glacier Retreat, Science, and Society, B.S. Orlove, E. Wiegandt, and B. Luckman, eds. University of California Press, Berkeley, CA, pp. 19–205.

Bush, R.T., Sullivan, L.A., Burton, E.D., Johnston, S.G., Keene, A.F., Wong, V.N.L. and Mosely, L. 2010. Climate change impacts on acid sulfate soil landscapes. Proceedings of Earth, Energy and the Environment: 20th Annual VM Goldschmidt Conference, Knoxville, TN, June 13--18. Geochemical Society and European Society for Geochemistry.

Downing, B., 2011. Permafrost and Acid Rock Drainage. InfoMine.com Publications. http://technology.infomine.com/enviromine/ard/Permafrost/Permafrost_ARDweb.htm.

Lliboutry, L., 1956. Nieves y Glaciares de Chile: Fundamentos de Glaciología. Editorial Universitaria, Santiago, Chile.

Lliboutry, L., 1961. Phénomènes cryoniveaux dans les Andes de Santiago (Chili). Biuletyn Peryglacjalny, vol. 10, pp. 209–224.

Lliboutry, L., 1986. Rock glaciers in the dry Andes. Data of Glaciological Studies (MGI), vol. 58, pp. 18–24; 139– 144.

Nordstrom, D.K., 2009. Acid rock drainage and climate change. Journal of Geochemical Exploration, vol. 100, pp. 97–104.

Ripley, E.A., Redman, R.E., and Crowder, A.A., 1995. Environmental Effects of Mining. CRC Press/St. Lucie Press, Boca Raton, FL.

U.S. Environmental Protection Agency, 2001. Abandoned Mine Site Characterization and Cleanup Handbook. EPA 530–C–01–001. U.S. EPA, Seattle, WA.

16
Acid Sulfate Soils

JAMES A. JACOBS

The characteristics of acid sulfate soils have been known by farmers in northern Europe for hundreds of years. According to a history of acid sulfate soils (Fanning et al., 2006), the earliest acid sulfate soils were recognized scientifically in the Netherlands by a Swedish taxonomist and botanist, Carl Nilsson Linnaeus (1707–1778), known to the scientific world by his Latin name, Carolus Linnaeus, and following his ennoblement in 1761 as Carl von Linné. Linnaeus called these soils *argilla vitriolacea*, meaning "clay with sulfuric acid" (Dost, 1973). Acid sulfate soils were subsequently recognized in other parts of northern Europe and given the Dutch name *Kattekleigronden*, described in the English soil science literature as "cat clay." Acid sulfate soils were recognized under the name "cat clays" in the United States in the 1950s and 1960s, ago, the decades Introduction U.S. Soils Conservation Service noted that acid-producing marsh sediment areas identified on coastal plains should not be disturbed, if possible. It was noted at the time that no attempt should be made to develop or reclaim such areas and that the best land-use planning strategy would be to use such tracts as wildlife refuges (Fanning et al., 2006). Acid sulfate soils were known in northern European countries for their acidity and strange reddish-orange color, reflecting oxidized conditions of iron and sulfur compounds. It was not lost on early Benelux farmers that wetlands and marshes containing these soils were difficult to convert to agricultural lands. Fanning et al. (1993) documented the colors of acid sulfate soils. Local words were developed to describe the strange qualities of these low-pH soils. *Maibolt* was a term for "hayfields under the influence of an evil spirit or the devil," and in Germany, *Gifterd*e referred to soils containing "poison earth" (Pons and Zonneueld, 1965; Benzler, 1973; Pons, 1973). The technical term *acid sulfate soils* was first used at the first international acid sulfate soils symposium in 1972 (Fanning et al., 2006). In an early study of acid sulfate soils, Edelman and van Staveren (1958) studied marsh soils in the United States and in the Netherlands.

The cat clays in northern Europe became identified with tidal marsh soils and land reclaimed from the sea (polders and associated soils) that had accumulated sulfide minerals during deposition of the soil and sediments through the reduction of sulfate from seawater by an overall process that may be referred to as *sulfidization* (Fanning and Fanning, 1989; Fanning et al., 2002), or *pyritization* (Rickard, 1973).

Similar acid-generating soils were found and documented in Thailand, Senegal, Gambia, Viet Nam, and other coastal areas. Research into acid sulfate soils and the humid tropics was presented in Indonesia (Agency for Agricultural Research and Development, 1990). The genesis, morphology, and classification of acid sulfate soils in coastal plains was documented by Van Breemen (1982). Acid sulfate soils may also occur at higher elevations and inland, in waterlogged and anaerobic soils where sulfur and iron are available to reducing bacteria. These environments include swamps, groundwater discharge zones or seeps, and historic mine properties.

In Australia, soils high in iron sulfide concentrations have been mapped along the coastlines of the Northern Territory, Queensland, and New South Wales. Acid sulfate soils and the associated acid generation problems have also been observed in some of the eastern coastal states of the United States. In Virginia and Maryland, near-surface acid sulfate soils that contain unoxidized pyrite at shallow depths have been disturbed in the process of building housing tracts and highway projects where the soils contain unoxidized pyrite. Acid rock drainage from highway and construction activities in Virginia was noted by

Daniels and Orndorff (2003). Grass et al. (1962) studied submerged and reclaimed sediments of the San Francisco Bay system on the west coast of the United States. Even inactive dredge stockpile areas have been noted to become sources of acid drainage, years after the original dredging operation occurred and the dredge spoils were deposited (Fanning et al., 2006).

Visual cues to the acid drainage associated with pyrite oxidation includes dead vegetation or the general lack of vegetation fish kills and other dead aquatic organisms. In developed areas where concrete or other porous surfaces are present in acid drainage areas, road and sidewalk surfaces may be coated with the noticeable reddish-orange iron hydroxide stain. Examples of numerous detailed field logs of acid sulfate soil sections have been provided by Fanning et al. (2006).

The U.S. Department of Agriculture Soil Survey Staff wrote a series of important soil papers regarding soil classification, discussing acidic soils (1960, 1970, 1975, 1992, 1999, and 2003). According to Fanning et al. (2006) for soil classification, the U.S. Department of Agriculture (USDA) split the acid sulfate soils into sulfidic and sulfuric categories, which were first officially recognized, as were the great groups Sulfaquents and Sulfaquepts, in the USDA Soil Taxonomy (Soil Survey Staff, 1975). Soil taxonomy has been summarized by Fanning and Witty (1993). The special characteristics of the weathering of acid sulfate soils was examined by Kittrick et al. (1982).

Australian soil scientists have developed a useful system of acid sulfate soil characterization (Thomas et al., 2003). In areas where acid sulfate soils possibly exist, all disturbances to the groundwater hydrology or surface drainage patterns that exist below about 15 ft, should be investigated, designed, and managed to avoid potential adverse effects of the acid sulfate soils on the natural and developed environment (Dear et al., 2002). When undisturbed and saturated by water, acid sulfate soils remain relatively benign and are considered potential acid sulfate soils. Potential acid sulfate soils are environmentally unfriendly soils when they are exposed to air by disturbance or overdrainage and then rewetted. When this occurs they become strongly acidic ($pH < 3.5$), and acid drainage water is produced. This acid, together with toxic elements that are leached from sediments, can kill fish and contaminate shellfish, drinking water, and groundwater. It can also corrode concrete and steel in homes, underground pipes, and buildings, where it is inadequately neutralized by the receiving environment.

Actual acid sulfate material can be identified in the field as the sulfuric horizon frequently found in coastal sedimentary soils that once contained iron sulfides, primarily pyrite, and may still contain some, but which has been exposed to the atmosphere by drainage or disturbance so that the pyrite has oxidized to form sulfuric acid, thereby decreasing the pH of the soil to less than 3.5. Actual aid sulfate soils are also characterized by bright yellow or straw-colored mottles of the mineral jarosite and often contain dark reddish streaks of iron oxide. Potential acid sulfate material is a coastal sedimentary sequence that contains iron pyrites that have not been oxidized. Consequently, the pH is approximately 7 (Thomas et al., 2003).

Disturbing Acid Sulfate Soils

In infrastructure or construction projects involving the possible disturbance of acid sulfate soils, the risk associated with the activities must first be assessed through consideration of both on- and off-site effects. The investigation described here can be modified and used for acid mine drainage study areas as well. A thorough acid sulfate soil investigation is an essential component of risk assessment. Such an investigation is needed to provide information on the environmental setting, location of and depth to acid sulfate soil, existing and potential acidity present in the soil, and soil characteristics. A best management practices strategy for a site is developed from the acid sulfate soil investigation. Successful management of acid

sulfate soils depends on implementing a realistic acid sulfate soil management plan (Thomas et al., 2003).

The first step in acid sulfate soil management is to determine whether acid sulfate materials are present on the site. An environmental site assessment is the first step in acid sulfate soil evaluation and relies on data supplied by others, including public and private sources. Environmental regulatory agencies and geological surveys should be contracted to verify existing published acid sulfate soil maps and reports. The environmental site assessment should be followed by field assessments, including preliminary field tests, such as field pH, the field peroxide test, and the field sulfate test.

Detailed soil and water sampling and laboratory analysis may be required at the detailed assessment stage to validate the likely environmental risks of undertaking a development or construction project, for example. Field inspection and sampling will include a large variety of field parameters, including (but not limited to) depth to water; pH of soils at various depths; detailed lithological descriptions; visible staining of reds, oranges, or yellows in the surface water or in the soils; dead vegetation; or dead organisms.

The geochemistry of the water should be measured in the field with calibrated meters. Most multimeters have dissolved oxygen, oxidation--reduction potential, pH, temperature, and conductivity. Most aquatic organisms can cope with a pH range of 5.5 to 8.5, but a pH of 6.5 to 8.0 is optimal. Freshwater streams or lakes range in conductivity from 50 to 1500 µS/cm, and the optimum conductivity range to support diverse aquatic life is 150 to 500 µS/cm. For dissolved oxygen, 0 to 2 mg/L is considered hypoxic and is not enough oxygen to support most aquatic life, freshwater or marine, except jellyfish, which can survive at dissolved oxygen at levels as low as 1.3 mg/L. Dissolved oxygen of 2 to 4 mg/L is low, and only a few fish and aquatic insects can survive at these levels. Dissolved oxygen of 4 to 6 mg/L is within the healthy range for many aquatic organisms. A dissolved oxygen level greater than 6 mg/L is excellent for most fish and aquatic organisms.

Natural levels of nitrate are usually less than 1 mg/L; however, for nitrate-sensitive fish such as salmon, the recommended maximum nitrate concentration is 0.06 mg/L. In general, concentrations of phosphates of over 0.05 mg/L will probably have an impact on freshwater streams and lakes, while concentrations of phosphates greater than 0.1 mg/L will affect river and lake environments. For an acid sulfate soil management plan, compliance points in various locations might be established with goals for pH, dissolved oxygen, and other parameters. For example, the goals might be set for daily monitoring, and the overall pH must be greater than 5.5, with total dissolved solids below 1250 mg/L, total suspended solids below 50 mg/L, total iron below 0.5 mg/L, and total aluminum below 0.06 mg/L for pH 6.0. The goals may vary based on the compliance location. Detailed regulatory requirements will dictate the environmental compliance goals.

Acid sulfate soil management guidelines have been summarized by Thomas et al. (2003) and should be applied following the management principles developed by Dear et al. (2002):

1. Minimize the acid generation potential by avoiding the disturbance of acid sulfate soils. This is the least costly and best management practice with the fewest potential environmental impacts.
2. Where disturbances of acid sulfate soils are unavoidable, the preferred management strategies are:
    - Minimization of the disturbance.
    - Neutralization of the acidic soils by liming. Using enough calcium carbonate to get the pH of the postoxidized soil up to about 5.5 or 6.0 (e.g., 50 kg of lime per ton of acid sulfate soil).
    - Hydraulic separation of sulfides either on its own or in conjunction with dredging. The extraction

of pyrite might be accomplished using a cyclonic separator on sandy soils, and the finer materials could be reburied.

- Strategic reburial or encapsulation.

Other management measures may be considered but must not pose unacceptably high risks. The main preferred management of acid sulfate soils matches closely the best management practices for acid mine drainage for coal and hardrock mining operations.

3. Field projects should be designed and implemented using best management practices when it has been demonstrated that the potential effects involving acid sulfate soils are manageable, to ensure that potential short- and long-term impacts on the environmental are minimized.
4. The material being disturbed, including the in situ acid sulfate soil and any potentially contaminated acidic waters associated with the acid sulfate soil disturbance, must be evaluated when developing a management plan for acid sulfate soils and in complying with the general regulatory requirements and guidelines.
5. As noted by the U.S. Environmental Protection Agency, dilution is not a remediation method. Marine, estuarine, brackish, or fresh waters are not to be used for diluting or neutralizing acid sulfate soils or associated contaminated waters.
6. In areas where regulatory guidelines or acid sulfate soils action criteria have been established and the levels have been reached or exceeded, active management of disturbed acid sulfate soils is to occur to remedy the situation and minimize the potential acid generation.
7. Stockpiling of untreated acid sulfate soils above the permanent groundwater table with or without containment is not an acceptable long-term management strategy. For example, in soils that are to be stockpiled, disposed of, used as fill, placed as temporary or permanent cover on land or in waterways, sold or exported off the treatment site or used in earth bunds, those that exceed the regulatory guidelines or action criteria should be actively managed and treated.
8. The following issues should be considered when formulating acid sulfate soil environmental management plan and site-specific strategies:
    - The sensitivity of the receiving environment
    - The exposure pathways for acidic waters and possible metals
    - The likelihood that groundwater or surface waters will be directly or indirectly affected by the development activity proposed
    - The heterogeneity, geochemical, and textural properties of possible acid sulfate soils on-site
    - The management and planning strategies of local regulatory agencies

Precommencement monitoring methods for acid sulfate soils:

- An inspection protocol should be developed for excavation or acid sulfate soil exposure activities.
- Methods for on-site soil and water treatment and management should be defined in a management plan.
- Water leachate and waste acid sulfate soil quality goals for excavation, restoration, and postrestoration should be documented in the management plan.
- Postrestoration monitoring and case closure goals should be defined.

Best management practice requires the preparation of a comprehensive, technically valid, and verifiable soil management plan, which should include:

- Detailed site investigation into soil hazards
- Establishment of baseline environmental conditions
- Selection of appropriate treatment options
- Laboratory and field validation demonstration trials
- Specification of ongoing monitoring and compliance
- Specification of contingency remediation

As an example of an acid sulfate soil management plan, actual acid sulfate soils might be defined as generally having a field pH of 4 or less, and potential acid sulfate soils might be defined using the hydrogen peroxide test, a change in color from gray to brown tones, effervescence, the release of sulfur-smelling gases, the lowering of pH by at least 1 unit, and a final pH of below 3.5, preferably below 3.0. For a disturbance of more than a specific amount of volume or weight, for example, 500 tons, an oxidizable sulfur content of a certain percentage, such as 0.02 or 0.03%, might be defined as the compliance target or regulatory limit. Other laboratory tests, such as the equivalent total potential acidity or total actual acidity, might be used in an acid sulfate soil management plan as a compliance target.

Acid Sulfate Soils and Global Climate Changes

Generation of waste piles and possible leachate from acid sulfate soils during a project should be monitored to confirm the effectiveness of the processing methods. This would include the sulfur content of the waste soils removed, and concentration of oxidizable sulfur that will remain buried in the saturated zone. Changes in recent global climate might affect water levels, as yearly fluctuations in the groundwater or surface water level may be larger than in the past. These fluctuations may bury actual and potential acid sulfate soils beneath water in areas of rising sea level, and in other shallow soil areas, lowered surface water might expose iron sulfide minerals to oxidizing conditions due to drier conditions in certain parts of the world. In addition, groundwater tables might be lowered due to increased reliance on groundwater and heavier groundwater pumping. This lowering of the water table exposes pyrite to potential oxidation.

Best Management Practices for Acid Sulfate Soils

Best practice requires formulation of effective, cost-efficient, and environmentally acceptable soil management techniques for development and construction activities. The daily pH values of removed surface water or leachates from a processed sand stockpile will indicate the sulfur content and may trigger additional testing for the acid sulfate soil management plan. Use of an independent, third-party environmental consultant, usually a professional geologist, soil scientist, or engineer, is recommended to monitor and document site conditions during acid sulfate soil disturbance activities and postconstruction monitoring, using a regulatory-approved acid sulfate soil management plan for the field guidelines.

In some acid sulfate soils, sufficient neutralizing material, usually shell or calcium carbonate, is present to maintain a high pH. Laboratory methods to evaluate acid sulfate soils have been noted by Ahern et al. (2004). Estimating lime requirements using a modified hydrogen peroxide potential acidity process was described by Barnhisel and Harrison (1976) and is a reasonable method for determining lime needs on an

acid sulfate soil project.

Summary

Acid sulfate soils are typically coastal, maritime, and located in humid tropical or temperate climates. Although many are found in rural areas, as more urbanization occurs along coastal areas, with development within acid sulfate soils, it is becoming a larger problem, especially for foundations and urban infrastructure. Inappropriate disturbance of acid sulfate soils can generate large amounts of sulfuric acid and leaching of metals and other contaminants that are naturally occurring in the soils. Flushing of acidic leachate to groundwater and surface waters can cause off-site impacts, including:

- Ecological damage to aquatic and riparian ecosystems
- Effects on estuarine fisheries and aquaculture projects
- Contamination of groundwater with aluminum, lead, arsenic, and other heavy metals
- Reduction in agricultural productivity through metal contamination, predominantly by aluminum and arsenic
- Damage to infrastructure through the corrosion of concrete and steel pipes, bridges, and other subsurface assets
- Generally, non-point-source pollution

To minimize the impacts of acid sulfate soils requires best management practices outlined by Thomas et al. (2003) and in other publications. Prior to development, accurate mapping of the presence of acid sulfate soils and potential acid sulfate soils precludes subsurface surprises during construction projects. Planning also includes acid sulfate soil management plans and best management practices for the site-specific area and local regulatory agencies. During construction, active documentation and monitoring of changing geochemical conditions is important. Postdevelopment monitoring is also necessary. If acid generation begins, minimization of the impacts occurs if contractors are prepared for mitigation responses.

References and Suggested Reading

Agency for Agricultural Research and Development and Land and Water Research Group, 1990. Presented at the Workshop on Acid Sulphate Soils in the Humid Tropics, Bogar, Indonesia, November 20–22.

Ahern, C.R., McElnea, A.E., and Sullivan, L.A., 2004. Acid Sulfate Soil Laboratory Methods Guidelines. Queensland Department of Natural Resources, Mines and Energy, Indooroopilly, Queensland, Australia, 186 pp.

Barnhisel, R.I., and Harrison, J., 1976. Estimating Lime Requirement by a Modified Hydrogen Peroxide Potential Acidity Method. Unpublished method for the Kentuckey Agricultural Experiment Station. Soil Testing Laboratory, Lexington, KY.

Benzler, J.H., 1973. Probleme bei der Kartierung von “Maibolt” and “Pulvererde”—besonderen Formen der Sulfatesauren Böden—in den Marschgebieten Niedersachsen.

Daniels, W.L., and Orndorff, Z.W., 2003. Acid rock drainage from highway and construction activities in

Virginia, USA. In: Proceedings of the 6th International Conference on Acid Rock Drainage. Cairnes, Queensland, Australia, C. Bell, ed. Australian Institute of Mining and Metallurgy, Carlton, Victoria, Australia, pp. 479–487.

Dear, S.E., Moore, N.G., Dobos, S.K., Watling, K.M., and Ahern, C.R., 2002. Soil management guidelines, version 3.8. In: Queensland Acid Sulfate Soil Technical Manual. Department of Natural Resources and Mines, Indooroopilly, Queensland, Australia, 63 pp.

Dost, H., ed., 1973. Acid sulphate soils. In: Proceedings of the First International Symposium, Wageningen, The Netherlands, August 13–20, vol. I and II. Publication 18. International Land Reclamation Institute, ILRI. Wageningen, The Netherlands.

Dost, H., ed., 1988. Selected Papers of the Dakar Symposium on Acid Sulphate Soils, Dakar, Senegal, January 1986. ILRI Publication 44. International Land Reclamation Institute, Wageningen, The Netherlands.

Dost, H., and van Breemen, N., eds., 1982. Proceedings of the Bankok Symposium on Acid Sulphate Soils, January 18–24. ILRI Publication 31. International Land Reclamation Institute, Wageningen, The Netherlands.

Edelman, C.H., and van Staveren, J.M., 1958. Marsh soils in the United States and in the Netherlands. Journal of Soil and Water Conservation, vol. 13, no. 1, pp. 5–17.

Fanning, D.S., 2002. Acid sulfate soils. In: Encyclopedia of Soil Science, R. Lal, ed. Marcel Dekker, New York, pp. 11–13.

Fanning, D.S. and Fanning, M.C.B., 1989. Soil: Morphology, Genesis, and Classification. Wiley, New York, 395 pp.

Fanning, D.S., and Witty, J.E., 1993. Revisions of soil taxonomy for acid sulfate soils. In: Selected Papers of the Ho Chi Minh City Symposium on Acid Sulfate Soils, M.E.F. van Mensvoort and D.L. Dent, eds. ILRE Publication 53. International Land Reclamation Institute, Wageningen, The Netherlands, pp. 61–69.

Fanning, D.S., Rabenhorst, M.C., and Bigham, J.M., 1993. Colors of acid sulfate soils. In: Soil Color, J.M. Bigham and E.J. Ciolkosz, eds. SSSA Special Publication 31. Soil Science Society of America, Madison, WI, pp. 91–108.

Fanning, D.S., Rabenhorst, M.C., Burch, S.N., Islam, K.R., and Tangren, S.A., 2002. Sulfides and sulfates. In: Soil Mineralogy with Environmental Applications, J.B. Dixon and D.G. Schulze, eds. Soil Science Society of America, Madison, WI, pp. 229–260.

Fanning, D.S., Rabenhorst, M.C., and Sullivan, L.A., 2006. Some history of the recognition about acid sulfate soils---internationally, and in the United States. In: Acid Sulfate Soils of the U.S. Mid-Atlantic/Chesapeake Bay Region, Tour, Guidebook, Tour, July 6–8, D.S. Fanning, ed. For the 18th World Congress of Soil Science, Philadelphia, PA, pp. 5–23.

Grass, L.B., Aronovici, V.S., and Muckel, D.C., 1962. Some chemical characteristics of submerged and reclaimed sediments of the San Francisco Bay system. Soil Science Society of America Proceedings, vol. 26, pp. 453–455.

Kittrick, J.A., Fanning, D.S., and Hossner, L.R., 1982. Acid Sulfate Weathering. Soil Science Society of

America, Special Publication 10. Madison, WI, 234 pp.

Pons, L.J., 1973. Outline of the genesis, characteristics, classification and improvement of acid sulphate soils. In: Proceedings of the 1972 (Wageningen, Netherlands) International Acid Sulphate Soils Symposium, Vol. 1, H. Dost, ed. ILRI Publication 18. International Land Reclamation Institute, Wageningen, The Netherlands, pp. 3--27.

Pons, L.J., and Zonneveld, I.S., 1965. Soil Ripening and Soil Classification. ILRI Publication 13. International Land Reclamation Institute, Wageningen, The Netherlands.

Rickard, D.T., 1973. Sedimentary iron sulfide formation. In: Proceedings of the 1972 (Wageningen, Netherlands) International Acid Sulphate Soils Symposium, Vol. 1, H. Dost, ed. ILRI Publication 18. International Land Reclamation Institute, Wageningen, The Netherlands, pp. 28--65.

Soil Survey Staff, 1960. Soil Classification: A Comprehensive System, 7th Approximation. U.S. Department of Agriculture, Washington, DC.

Soil Survey Staff, 1970. Selected Chapters from the Unedited Text of the Soil Taxonomy of the National Cooperative Soil Survey. U.S. Department of Agriculture, Soil Conservation Service, Washington, DC.

Soil Survey Staff. 1975. Soil Taxonomy. USDA Handbook 436. U.S. Department of Agriculture, Washington, DC.

Soil Survey Staff, 1992. Keys to Soil Taxonomy, 5th ed. USDA Soil Management Support Services Technical Monograph 19. Pocahontas Press, Blacksburg, VA.

Soil Survey Staff, 1999. Soil Taxonomy, 2nd ed. USDA Handbook 436. U.S. Department of Agriculture, Washington, DC.

Soil Survey Staff. 2003. Keys to Soil Taxonomy. 9th ed. U.S. Department of Agriculture, Natural Resources Conservation Service, Washington, DC.

Thomas, B.P., Fitzpatrick, R.W., Merry, R.H., and Hicks, W.S., 2003. Acid Sulfate Soil Technical Manual (Version 1.2): Coastal Acid Sulfate Soil Management Guidelines. CISRO Land and Water, Canberra, Australia, 65 pp.

Van Breemen, N., 1982. Genesis, morphology, and classification of acid sulfate soils in coastal plains. In: Acid Sulfate Weathering, J.A. Kittrick, D.S. Fanning, and L.R. Hossner, eds. Soil Science Society of America, Madison, WI, pp. 95–108.

17
Prevention of Arsenic Mobilization related to Sulfide Oxidation in Aquifers

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Pyrite oxidation is the core issue associated with acid mine drainage and acid sulfate soils. Sulfide oxidation is also the main biogeochemical reaction that occurs when surface waters such as storm waters carry dissolved oxygen at concentrations of 6 to 8 mg/L into naturally anaerobic aquifers. In such cases, arsenic and other metals that are commonly associated with sulfur deposits can be solubilized as the pyrite is oxidized to yield iron oxyhydroxides, sulfate ions, and a lower pH.

Introduction

Arsenic is a ubiquitous element on Earth, mobilized through a combination of natural processes such as weathering and erosion, biological activity, and volcanic emissions. Human activities can also change redox conditions in aquifers to release heavy metals, including arsenic. Arsenic occurs as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulfides, oxides, arsenites, and arsenates. Most are ore minerals or their alteration products, and among arsenic-containing compounds in ore zones are arsenian pyrite [$Fe(S,As)_2$], arsenopyrite (FeAsS), realgar (AsS), orpiment (As_2S_3), cobaltite (CoAsS), niccolite (NiAs), and scorodite ($FeAsO_4 \cdot 2H_2O$). Pyrite is not stable in aerobic systems and oxidizes to iron oxides with the release of significant amounts of sulfate and acidity and associated trace metal constituents, including arsenic (Smedley and Kinniburgh, 2005). Table 17.1 summarizes the typical ranges of arsenic in common sulfur and iron compounds.

Table 17.1 Typical Ranges of Arsenic Concentrations in Common Rock-Forming Minerals Associated with Sulfur and Iron

Mineral Category	Mineral	Arsenic Concentration Range (mg/kg)
Sulfide	Pyrite	100–77,000
	Pyrrhotite	5–100
	Marcasite	20–126,000
	Galena	5–10,000
	Sphalerite	5–17,000
	Chalcopyrite	10–5,000
Sulfate	Gypsum/anyhdrate	<1–6
	Barite	<1–12
	Jarosite	34–1,000
Iron oxide	Hematite	Up to 160
	Fe(III) oxyhydroxide	Up to 76,000
	Magnetite	2.7–41
	Ilmenite	<1

Source: After Smedley and Kinniburgh (2002).

Groundwater containing documented high levels of arsenic from sulfide-mineralized areas have been observed in numerous areas, including parts of the United States, Canada, southwestern England, Thailand, South Korea, Poland, Greece, Ghana, Zimbabwe, and Brazil. Typical groundwater conditions in mineralized mining areas are fractures in crystalline rocks or alluvial placer deposits. Oxidizing or mildly reducing conditions are possible, especially in porous shallow aquifers with infiltrating storm waters containing 7 to 8 mg/L dissolved oxygen. Worldwide, the groundwater from sulfide-mineralized areas or mining areas containing higharsenic concentrations also have ubiquitously high sulfate concentrations, which are typically hundreds of mg/L or higher. The sulfide-rich waters are usually acidic unless buffered by carbonate minerals, and these waters often have increased concentrations of other trace metals, such as Ni, Pb, Zn, Cu, and Cd (Smedley and Kinniburgh, 2005).

Arsenic has long been associated with sulfur ore mineralization and the release of arsenic into surface water or groundwater is associated with pyrite oxidation by iron- and sulfur-oxidizing bacteria. The highest arsenic concentration reported, 850 mg/L, is from an acid mine seep at Iron Mountain, near Mt. Shasta, California. The Iron Mountain acid drainage has pH values measured at −3.6 (Nordstrom and Alpers, 1999).

Aquifer Management, Pyrite Oxidation, and Arsenic

Reinjection of oxygenated waters into drinking aquifers can provide the necessary dissolved oxygen for iron- and sulfur-oxidizing bacteria to oxidize pyrite-generating sulfuric acid and releasing arsenic. If this process is not well planned, arsenic can be produced. Storage and recovery systems were originally designed in southern Florida. Variations in arsenic mobilization that have occurred within Florida have been observed (Pearce and Waldron, 2010). Because of arsenic mobilization problems, methods have been introduced to minimize arsenic mobilization, including the use of sulfides such as HS^- or S^{2-} to

prevent the mobilization of arsenic at a site in DeLand, Florida.

Aquifer Storage and Recovery

Aquifer storage and recovery (ASR) is a term used to describe the injection of water into a subsurface aquifer for storage during periods when water is available with recovery at a later date when water is less available. An example of an ASR cycle in southern Florida would be the injection of 100 million gallons of water at 1 million gallons per day, followed by a storage period of one to four months. At the end of this period, when surface water resources are reduced due to lack of rain, the water is recovered as needed or to a water quality limit such as 250 mg/L chlorides, the current drinking water standard.

The ability to store and recover water below the surface resulted in the implementation of numerous ASR projects in Florida over the last three decades, as more and more utilities grew concerned about growing needs and dwindling supplies. ASR technology offers the ability to store potable water, partially treated surface water, and reuse water from wastewater treatment plants without the need to develop aboveground storage facilities.

By regulation, all water stored in the subsurface must meet primary drinking water standards when it is injected into an aquifer defined by the U.S. Environmental Protection Agency (EPA) as an *underground source* of *drinking water* (USDW), an aquifer containing less than 10,000 mg/L total dissolved solids. Federal regulations also require that the injected water not cause changes in the native formations which would result in concentrations of regulated chemicals to exceed primary drinking water standards or exceed native formation water quality if the concentrations in the native formation water exceed primary drinking water standards for a given parameter.

As the number of ASR projects increased in Florida and around the country, additional water analyses were required by the regulating bodies to further establish water quality in the injected and recovered water. Additional monitoring of arsenic levels was required between 2000 and 2004 since the EPA planned to lower the primary drinking water standard for arsenic from 50 µg/L to 10 µg/L. The new rule went into effect on January 1, 2005 in Florida and on January 1, 2006 nationally. Early reviews of 13 ASR sites indicated that arsenic levels in recovered water commonly exceeded the regulatory standard of 10 µg/l during the first cycle, but that arsenic levels often dropped below the 10 µg/L limit during additional cycles (Pyne et al., 2004). This information was based on a review of 12 ASR sites in Florida. As arsenic monitoring continued after 2006, it became clear that arsenic was a continuing problem at some sites in Florida (Llewellyn, 2008). To address the arsenic issue fundamentally, entities connected with the water resource industry in Florida began reviewing the literature for a broader understanding of the source of arsenic mobilization and the development of treatment alternatives where they were needed. Work by Stuyfzand (1998) showed that arsenic mobilization within subsurface aquifers is closely associated with the injection of oxygenated water into anoxic aquifers containing pyrite. Unfortunately, this observation is not sufficient to explain the different behaviors manifested by arsenic mobilization at different sites.

The behavior observed for mobilized arsenic varies between sites as enumerated below.

1. The maximum concentration of arsenic measured during recovery at different ASR wells varies. Initial arsenic concentrations range from below the detection limit of 3 µg/L to more than 90 µg/L.
2. The point during recovery when the maximum arsenic concentration is observed at ASR wells during cycle recovery varies. At some sites the maximum arsenic level occurs in the first few samples at the start of recovery. At other sites, the maximum value is reached at the end of recovery. A third type of behavior observed is represented by sites where the maximum arsenic level occurs at an intermediate

point during recovery.

3. A third difference between sites is how arsenic concentrations vary during recovery, At some sites arsenic concentrations decline rapidly during recovery and do not exceed regulatory levels during additional cycles. At other sites, little arsenic is recovered during the initial recovery cycle. However, arsenic levels begin low at the start of additional cycles but increase with recovered cycle volume. Finally, at one site, the arsenic level during three consecutive cycles increased at the very start of each recovery from an initial low of approximately 90 µg/L on the first cycle to a record high of almost 900 µg/L on the third cycle. At this site, arsenic concentrations declined to a steady level between 60 and 100 µg/L during the remaining stages of each recovery. Also, over 2.5 times the volume of water stored in the aquifer was required to be recovered before arsenic levels fell below 3 µg/L at this site.

The varied behavior observed for arsenic mobilization suggests that multiple reaction pathways are operating even though the dissolved oxygen content in the injected water and the arsenic content and location of the arsenic within the formations are similar. If it is assumed that the reaction rate associated with the basic reactions are probably similar, the variation in arsenic concentrations and behavior is probably associated with different formation flow properties, such as flow paths (heterogeneous vs. homogeneous) and dispersivity, injected water quality (presence or absence of organic materials), and other parameters that are more easily conceptualized than demonstrated.

Based on site-specific circumstances and the insights provided by Stuyfzand (1998), the water resource industry began to address arsenic mobilization following four different approaches that were partially dependent on the site. For sites where arsenic did not rise above regulatory standards, additional monitoring was required. For some sites that were continuing to experience arsenic at elevated levels, additional cycles were undertaken and additional monitoring wells were sometimes required. These sites appear to be operating under the assumption that arsenic could be completely leached from the formation after an unspecified number of cycles (CH_2M Hill, 2007). The third approach was designed to remove the dissolved oxygen from the water using a membrane technology (Kohn, 2009) or catalytic removal using hydrogen and a palladium catalyst (Entrix, 2009a--c). Finally, a fourth approach was undertaken in response to the difficulties encountered by the membrane and catalytic treatments. The fourth treatment method was based on the addition of sulfides (HS^- and S^{2-}) in the form of sodium bisulfide (NaHS), since the NaHS could both react with dissolved oxygen and would chemically oppose the dissolution of pyrite (Pearce and Waldron, 2010).

Prevention of Arsenic Mobilization

Natural attenuation is probably associated with the formation of iron oxyhydroxides that adsorb and bind arsenic and represented by sites where arsenic levels fall below regulatory limits within a few cycles. In the absence of sulfide ions or other ions capable of reducing the iron, it is likely that the arsenic will remain trapped within these oxides (Pearce, 2005).

Leaching Process

It has been suggested that the arsenic in a formation may be removed completely by leaching arsenic from a formation using multiple ASR cycles and high oxidant concentrations (CH_2M Hill, 2007). This expectation appears unlikely. As an example, the Florida Department of Environmental Protection has estimated that an average concentration of arsenic in Florida's aquifer matrices utilized for storing water

is on the order of 3 mg/kg of formation (Haberfeld, 2009). Further, the bulk, if not all, appears to be bound in the pyrite located within the matrix pore spaces (Price and Pichler, 2005). A simple mass balance analysis shows that 12 billion gallons of water would need to be cycled through an aquifer to remove all of the arsenic from a pore volume of 100 million gallons, assuming that the concentration of arsenic in the recovered water remains constant at 50 µg/L and that the formation contains 3 mg of arsenic per kilogram of formation (Pearce and Waldron, 2010). The potential to leach all of the arsenic from a formation based on this analysis appears to be an unrealistic expectation.

Physical Methods for Removing Oxygen

In the event that either arsenic levels do not fall below regulatory levels in the water recovered after a few ASR cycles, or the performance of several cycles does not appear to be a workable approach to minimizing arsenic mobilization at a given site, it is reasonable to expect that other methods for limiting arsenic mobilization would be reviewed. Since oxidants in the injected water appear to play a major role in arsenic mobilization, methods designed to remove the oxidants from the injected water might be expected to reduce the amount of arsenic that may be mobilized at new sites or sites experiencing continued elevated arsenic concentrations. A brief review of generally available information indicates that two physical systems are available to remove oxygen from the injected water: (1) a nitrogen degasification system employed to remove oxygen from water, as used by the offshore oil and gas industry; and (2) a membrane degasification system, as used by the food and beverage industry, the semiconductor industry, and other industries, including those concerned with corrosion due to dissolved oxygen. Although both methods can successfully remove oxygen to very low levels, cost and operational issues must also be considered.

The nitrogen degasification system was reported to cost approximately $1 million in capital equipment for the construction of a 1-million gallon per day system (Pearce, personnel communication from vendor, 2005). This cost was considered beyond the budget tolerance of most utilities for this type of system and was not pursued further. The membrane system provided by Membrana, Inc. to remove oxygen appears to provide adequate oxygen removal but suffers from plugging of the membranes (Kohn, 2009).

Catalyzed Removal of Oxygen

Catalytic removal of dissolved oxygen using a palladium surface and dispersed hydrogen gas is also a potential oxygen-removing process. However, initial miniscale pilot test results performed for the St. Johns River Water Management District (SJRWMD) and the city of DeLand, Florida, indicated that the efficiency of the palladium catalyst to remove oxygen declined rapidly and did not suggest favorable long-term performance (Entrix, 2009c).

Chemical Removal of Oxygen Using Sulfide

Due to the capital costs and operational issues associated with the treatment options mentioned earlier, a sulfide treatment was developed for recharge water based on the following principles:

1. As indicated by the reaction

$$HS^- + 2O_2 \rightarrow H^+ + SO_4^{2-} \tag{17.1}$$

sulfides and oxygen can react to form sulfate ions. Therefore, the introduction of sulfides into the injected water would diminish the amount of oxygen available to react with pyrite in the target storage formation.

2. Sulfides provide a second line of defense against arsenic release in anoxic aquifers:

$$FeS_2 + H_2O \rightleftharpoons Fe^{2+} + 1\tfrac{3}{4}HS^- + \tfrac{1}{4}SO_4{}^{2-} + \tfrac{1}{4}H^+ \quad (17.2)$$

In this case, sulfides are able to suppress the dissolution of pyrite based on Le Châtelier's principle of equilibrium. This reaction also represents the natural equilibrium condition in the subsurface involving sulfides, sulfates, iron, pH, and pyrite.

To evaluate the ability of sulfides to prevent the mobilization of arsenic, it is relevant to review the potential pathways leading to the release of arsenic within the subsurface and to establish a reaction rate between sulfides and dissolved oxygen within the injected water. The following reaction provides an indication of the chemical reactions occurring in the subsurface when oxygenated water is introduced into a formation containing pyrite:

$$4FeS_2 + 14H_2O + 15O_2 \rightleftharpoons 4FeO(OH) + 8SO_4{}^{2-} + 16H^+ \quad (17.3)$$
$$\text{arsenic bound to pyrite} \rightleftharpoons \text{arsenic bound to FeO(OH)}$$

It is instructive to note that the iron in reaction (17.3) is oxidized from the 2+ oxidation state to the 3+ oxidation state (Usher et al., 2004), whereas the written reaction between dissolved oxygen and pyrite often suggests that only the sulfides in pyrite are oxidized during this reaction (Price and Pichler, 2005).

The secondary reaction immediately below (17.3) shows that arsenic, which is bound to the pyrite as a trace metal, is oxidized and then adsorbed by the iron oxyhydroxide formed during the reaction of pyrite with the oxygen. In this reaction, the arsenic is unlikely to be mobilized to any significant extent if the reaction occurs within a zone where the water is not moving rapidly (flow through a porous medium). However, in zones of fast-moving water, such as along fractures, arsenic may not have time to bind to the newly formed iron oxyhydroxides. The reaction that occurs during recovery when naturally occurring sulfides in the native water contact the iron oxyhydroxide formed during the injection of water containing dissolved oxygen is

$$8FeO(OH) + 9HS^- \rightleftharpoons 8FeS + SO_4{}^{2-} + 5H_2O + 7OH^- \quad (17.4)$$
$$\text{arsenic [trace in FeO(OH]} \rightleftharpoons \text{arsenic (mobilized)}$$

In this case, the sulfides in the native water react with the iron oxyhydroxides to produce iron sulfide. As the iron oxyhydroxides are reduced by the sulfides, the formerly bound arsenic moves into solution (Fendorf and Tufano, 2008).

Sulfide Injection System

When the catalytic process failed to produce positive results for deoxygenating the water in the minitest, the SJRWMD was interested in pursuing other options for preventing arsenic release. At this point, Cardno-Entrix proposed the use of sulfide compounds (NaHS or other soluble group I or group II metals) to prevent arsenic mobilization based on preliminary testing and theoretical concepts for deoxygenation that they had been evaluating. The basic premise was that the addition of low concentrations of sulfides would make the injected water more similar chemically (chemical and oxidation--reduction conditions) to the native water in the target storage zone. In turn, the sulfides would prevent or limit the formation of iron oxyhydroxides and therefore limit arsenic mobilization.

Two major technical issues needed to be evaluated under field conditions to confirm that sulfides would limit arsenic mobilization. The information required concerned the kinetic reaction rate between sulfides

and dissolved oxygen and the actual attenuation of arsenic mobility under operating conditions. The first step was to perform a pilot test to evaluate the chemical rate of reaction.

Reaction Kinetic Testing

The rate of dissolved oxygen depletion in the presence of low concentrations of sulfides was investigated using an approximate 300-gal system with four sampling ports. The flow rates through the system were set at 0.5, 1.0, and 2.0 gal/min, which equate to retention times of 600, 300, and 150 min. Oxidation--reduction potentials and oxygen concentrations were measured for samples recovered from four sampling ports. The ports were located just prior to the introduction of sulfides, just after the introduction of sulfides, after 150 gal of system volume, and at the end of the 300-gal pathway (Pearce and Waldron, 2010). Although somewhat crude, the data (Figure 17.1), suggest that the decline in dissolved oxygen follows first-order kinetics with a half-life of approximately 2 h. The data also indicated that the half-life may be significantly lower in the presence of limestone. However, since the limestone was not characterized, such a conclusion would be premature (Pearce and Waldron, 2010).

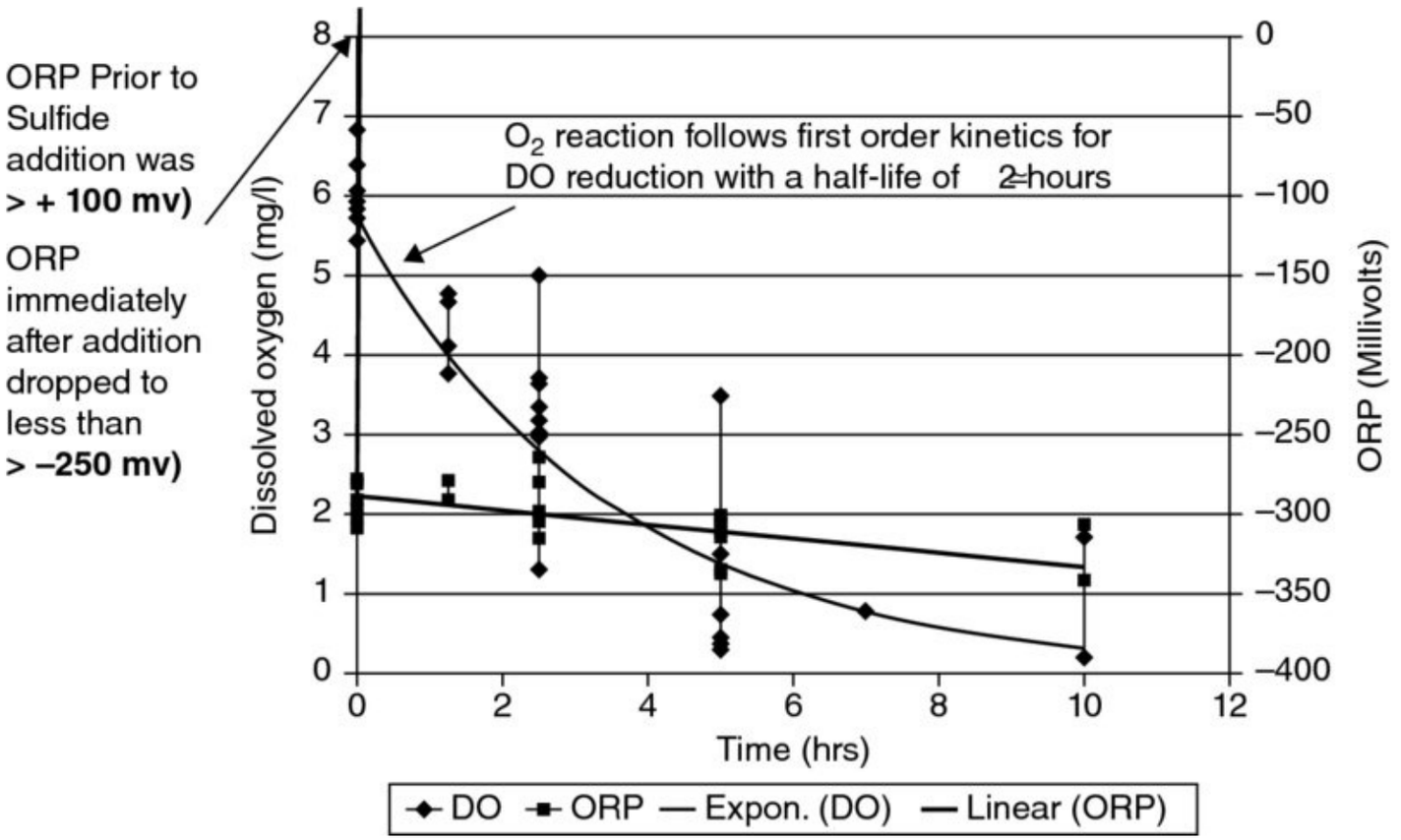

FIGURE 17.1 Dissolved oxygen and ORP levels measured during DeL and deoxygenation testing.

The conclusions that were drawn, based on the kinetic results for the decline of dissolved oxygen, were that (1) sulfides react to remove dissolved oxygen, (2) the reaction is not sufficiently rapid to prevent dissolved oxygen from entering the formation, and (3) dissolved oxygen will be reduced to insignificant levels within 24 h after entering the formation, based on the reaction half-life of 2 h at a sulfide concentration of 6 mg/L sulfides in the absence of any formation material.

The oxidation--reduction potential (ORP) data were somewhat clearer. Prior to the addition of sulfides, the ORP values were greater than 100 mV. However, immediately after the sulfides were added, the ORP value dropped to below −280 mV even though the dissolved oxygen concentration had not changed

(Pearce and Waldron, 2010). These results show that ORP values do not represent the final chemical environment of the water at equilibrium or the actual ORP level that will exist once equilibrium is reached.

Miniscale Pilot Testing

Based on the favorable results from the kinetics testing, the SJRWMD approved the construction and testing of a full-scale sodium bisulfide (NaHS) injection system at the DeLand, Florida site. The NaHS storage and chemical feed building was installed with secondary containment and simple metering equipment to control the NaHS concentration in the injected water.

After installation of the NaHS handling equipment, several miniscale pilot tests were performed by injecting water into the target ASR storage zone while varying the sulfide concentration for each test. To establish a baseline, two miniscale tests were performed without treating injected water with NaSH, two miniscale tests were performed using 2 ppm NaSH in the injected water, and two miniscale cycles were performed using 6 ppm NaSH. Finally, the last two test cycles, 7 and 8, were performed using 4 ppm NaSH. Cycle 7 was completed using an injected volume of 750,000 gal and the eighth cycle was performed using 5 million gallons. Tests results are provided in Table 17.2.

Table 17.2 Miniscale Test Results

Test Run	Cycle Volume (gal)	Sulfide Concentration (mg/L)	Average Arsenic Concentration (µg/L)	Maximum Arsenic Concentration (µg/L)
1	214,000	0	7.20	8.40
2	220,000	0	6.00	7.30
3	336,000	2	4.90	6.00
4	336,000	2	2.55	4.50
5	336,000	6	1.90	3.20
6	104,000	6	1.68	2.00
7	750,000	4	0.90	1.28
8	5,000,000	4	0.56	0.78
9	20,000,000	3.2	<0.5	1.30

The data in Table 17.2 show that more arsenic was mobilized when no sulfides were introduced than occurred when sulfides were introduced. It is recognized that the arsenic levels in the cycles that were not treated with NaHS remained below the regulatory limit, but it should be recognized that the cycle volumes were small and were utilized only to provide some insight into the potential for arsenic release at this site. Overall, the data indicated that sulfides could minimize arsenic mobilization and that further testing was warranted.

It is also relevant to note that the potential for capturing high levels of arsenic in the iron hydroxides, by injecting a large volume of water prior to running the testing with sulfides, warranted the use of lower volumes in the minicycles. It is worth noting that the stoichiometric concentration for the removal of oxidants was approximately 3.3 to 3.5 mg of sulfides per liter of water injected.

Preliminary Large-Scale Testing

Based on the success of the mini scale and 5-million gallon cycle testing, a preliminary large-scale test was performed. This test was designed to inject, store, and recover 20 million gallons. The results of a 20-million gallon test are also presented on line 9 of Table 17.2. It should be specified that the high value of 1.3 µg/L arsenic observed in this test was recorded in the sample recovered initially. No other samples indicated the presence of arsenic at concentrations above the detection limit of 0.5 µg/L.

Deoxygenating Groundwater and Precipitating Metals

Based on the data obtained during the testing performed during this project and presented in Table 17.2, it is reasonable to conclude that the addition of sulfides can limit the potential to mobilize arsenic during ASR and aquifer recharge projects. Other types of metal-immobilizing solutions used in the environmental remediation industry for at least two decades are shown in Table 17.3.

Table 17.3 Selected Reducing Compounds that Can Be Used for Deoxygenation

Selected Reducing Agents	**Phase and Possible Delivery Method**
Fe^0 [passive reactive barriers (PRBs)]	Placement in PRB
Carbon substrates: chitin, wood chips	Solids: PRBs, grout
Organic materials (water treatment sludge)	Solids: PRBs, grout
Colloidal Fe^0	Liquid or grout injection
Dithionite solution	Liquid: injection
Sodium sulfide	Liquid: injection
Calcium polysulfide	Liquid: injection
Sodium metabisulfite	Liquid: injection
Ferrous sulfate	Liquid: injection
Carbon substrates (edible soy oils, lactate, molasses, cheese whey, milk)	Liquids: injection
Hydrogen sulfide (H_2S, gas); infusion tools	Gas: infusion tools
Sulfur dioxide (SO_2, gas); infusion tools	Gas: infusion tools
Hydrogen (H, gas)	Gas: infusion tools
Carbon substrates (propane, butane, methane)	Gas: infusion tools

Reducing Agents

Reducing agents have been used in a variety of forms in the environmental remediation industry to address inorganic contaminants such as heavy metals. The reducing agents come as solids, liquids, and gas-phase reactants. The solid-phase reducing agents are usually injected with grout pumps or placed by backhoes or in specially designed wells. Liquids are injected using wells, probe rig injection ports, and even soaker hoses. Liquid-to-gas mass transfer devices are best used to maximize the solubility of a gas within a 2-in.-diameter or larger well (Jacobs et al., 2008). Although a powerful tool in water treatment, the use of reducing agents to modify redox chemistry in aboveground water treatment systems, surface water, or in an aquifer should be evaluated carefully in the laboratory prior to testing in the field, to prevent the mobilization of unwanted soluble metals or other entities releasing contaminants into the environment.

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References and Suggested Reading

CH_2M Hill, 2007. Arsenic Mobilization in Two Suwannee Limestone Aquifer Storage Recovery Systems. Southwest Florida Water Management District, Tampa, FL.

Entrix, 2009a. ASR Test Well and Monitor Wells Construction and Testing Report: City of DeLand Aquifer Storage and Recovery System, St. Johns River Water Management District (SJRWMD) ASR Demonstration Project. Report to SJRWMD.

Entrix, 2009b. Draft Technical Memorandum: Small-Scale Pilot Test of Catalytic Deoxygenation. Prepared for the St. Johns River Water Management District.

Entrix, 2009c. Technical Memorandum: City of DeLand Airport ASR Program, Mini-scale Pilot Test of Deoxygenation Using Sulfides. Prepared for the St. Johns River Water Management District.

Fendorf, S., and Tufano, K., 2008. Confounding impacts of iron reduction on arsenic retention. Environmental Science and Technology, vol. 42, pp. 4777–4783.

Haberfeld, J., 2009. Aquifer Recharge Projects in Florida. Presented at ASR 9. American Ground Water Trust, Orlando, FL.

Jacobs, J., Begley, J., and Murphy, N., 2008. Significant improvement of in-situ gas mass transfer performance for groundwater remediation projects. In: Battelle Conference, Abstract, Battelle Remediation of Chlorinated and Recalcitrant Compounds Meeting Proceedings, May 19–22, Monterey, CA.

Kohn, S., 2009. City of Bradenton Potable Water ASR Degas Pretreatment Pilot Study. Presented at ASR 9. American Ground Water Trust, Orlando, FL.

Llewellyn, J., 2008. Process for Regulating Aquifer Storage and Recovery Facilities (ASR) with Increased Levels of Arsenic. Program Guidance Document WRM/GW-08–01. Florida Department of Environmental Protection, Tallahassee, FL.

Nordstrom, D.K., and Alpers, C.N., 1999. Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund Site, California. Proceedings of the National Academy of Sciences, USA, vol. 96, pp. 3455–3462.

Pearce, M.S., 2005. Arsenic Mobilization in Florida's Aquifers: A Basic Perspective. Presented at ASR V. American Ground Water Trust, Tampa, FL.

Pearce, M.S., and Waldron, M. 2010. ASR Using Sodium Bisulfide for Deoxygenation to Prevent Arsenic Mobilization. Presented at the AGWT–AIPG Joint Conference, September, Orlando, FL.

Price, R.E., and Pichler, T., 2005. Abundance and mineralogic association of arsenic in the suwannee limestone (Florida): implications for arsenic release during water--rock interaction. Chemical Geology, vol. 228, pp. 44–56.

Puls, R.W., and Deutsch, W.J., 2000. Session 3 Summary: Redox proceses in inorganic remediation. In: Workshop on Monitoring Oxidation–Reduction Processes for Ground-water Restoration, Workshop Summary, Dallas, TX, April 25–27, R.T. Wilkin, R.D. Ludwig, and R.G. Ford, eds. Office of Research and Development, U.S. Environmental Protection Agency, Subsurface Protection and Remediation Division, National Risk Management Research Laboratory, Ada, OK, pp. 79–88.

Pyne, D., McNeal, M., and Horvath. L., 2004. Analysis of Arsenic Occurrence and Attenuation in Thirteen Operational ASR Wellfields in the Florida Hawthorn Aquifers. SJRWMD, Palatka, FL.

Smedley, P., and Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, vol. 17, pp. 517–568.

Smedley, P., and Kinniburgh, D.G., 2005. Arsenic in groundwater and the environment. In: Essentials of Medical Geology: Impacts of the Natural Environment on Public Health, O., Selinus, ed. Academic Press, San Diego, CA, pp. 263–299.

Stuyfzand, P.J., 1998. Quality changes upon injection into anoxic aquifers in the Netherlands: evaluation of 11 experiments. In: Artificial Recharge of Groundwater, J.H., Peters, et al., eds., A.A. Balkema, Rotterdam, The Netherlands, 474 pp.

Usher, C.R., Cleveland, C.A., Strongin, D.R., and Schoonen, M.A., 2004. Origin of oxygen in sulfate during pyrite oxidation with water and dissolved oxygen: an in-situ horizontal attenuation reflectance infrared spectroscopic isotope study. Environmental Science and Technology, vol. 38, no. 21, pp. 5604–5606.

PART III
PREDICTION AND PREVENTION OF ACID MINE DRAINAGE, ROCK DRAINAGE, AND SULFATE SOILS

18
Overview of Acid Drainage Prediction and Prevention

STUART R. JENNINGS AND JAMES A. JACOBS

Accurate prediction of acidic drainage from proposed mine projects is recognized by both industry and government as a critical requirement of mine permitting and long-term operation. Substantial emphasis has been placed on the prediction of acid drainage associated with coal development in the eastern United States (Brady et al., 1998; Skousen and Ziemkiewicz, 1996) and metal mining in the western United States and in Canada (Price, 2005; Maest et al., 2005; Kuipers et al., 2006). The standard protocols for evaluating geological materials for their ability to generate acid mine drainage are generally agreed upon within the scientific community, yet much uncertainty remains in the ability of scientists and engineers to predict the ultimate drainage quality years in the future, as many complex variables influence acid generation and neutralization. The backbone of predicting acid-generating potential from any geologic formation is the ability to characterize the presence and quantity of both acid-forming minerals and neutralizing minerals in the geological materials to be unearthed during mining operations.

Introduction

Typically, rock or soil samples are collected by drilling during exploration, analyzed, and interpreted with respect to their risk of acid formation. Methods for characterizing acid-forming minerals were developed during the 1970s in areas of the eastern United States mined for coal (Smith et al., 1974). Ultimately, these techniques lead to a standardized U.S. Environmental Protection Agency protocol for characterization of mine soil and overburden (Sobek et al., 1978). In these analytical approaches, the amount of sulfur present in geological materials is measured and attributed to being either an acid-forming mineral such as pyrite (FeS_2) or a non-acid-forming mineral such as gypsum ($CaSO_4 \cdot 2H_2O$). The relative amount of acid-forming minerals is then contrasted to the amount of neutralizing minerals such as calcite ($CaCO_3$) to develop a prediction of the probability of acid generation. The ratio of neutralization potential (NP) to acid potential (AP) is commonly presented in graphical interpretations, with the implication that geological materials with an abundance of NP are unlikely to generate acidic drainage.

In eastern coal mines, NP/AP ratios below 1 commonly produce acidic drainage, NP/AP ratios between 1 and 2 may produce either acidic or neutral drainage, and NP/AP ratios greater than 2 should produce alkaline water (Skousen et al., 2002). However, this index does not always accurately predict the resulting acid generation from a mine. Of 56 mines evaluated by Skousen et al. (2002), 11% did not conform to the results expected based on NP/AP ratios, including four sites with ratios above 2; these sites eventually produced acidic drainage. Furthermore, the applicability of the experimental findings from West Virginia coal deposits hosted in sedimentary rock to metal mines developed in igneous parent material is unknown. Sedimentary sulfide mineralization is caused by diagenetic interaction between microbes, Fe and S, in a low-temperature saturated environment, resulting in the formation of poorly crystallized pyrite, whereas igneous pyrite is formed by high-temperature magmatic fluids or molten rock cooling slowly to form well-developed crystalline structure. Mineralogical variation between each geologic domain causes dissimilar reactivity to weathering conditions and leads to laboratory variability in assessment. Recurrence of inaccurate interpretations between laboratory and field data has caused investigators to reexamine the adequacy of the analytical methods. Because of the challenges inherent in

interpreting laboratory data and predictive models, forecasting future water quality impacts from acid mine drainage should not be considered routine and robust; rather, they should be considered an area of uncertainty and ongoing research.

If the rates of weathering and availability of acid-forming and acid-neutralizing minerals are dissimilar, the potential exists that acid generation may overwhelm the pool of resident NP. Slowly reacting neutralizing minerals may lead to the generation of acidic water. Sherlock et al. (1995) evaluated the rates of weathering of sulfides, carbonates, and silicates and determined that sulfide minerals reacted fastest and cautioned that conventional methods of prediction do not consider that specific mineralogy and reaction kinetics are at risk of erroneous interpretations and predictions.

Overburden Analysis

The acid-generating potential of a mine site can be evaluated by sampling the overburden rock and soil, which will commonly end up as mine tailings or waste materials at a surface mine. These rock and soil samples, if representative of the sulfur content in these waste zones, can be used for acid–base accounting (ABA) tests. Acid–base accounting is the most commonly used method of overburden analysis. When performing ABA, the following information is required: (1) neutralization potential, (2) percent total sulfur (S), and (3) “fizz” testing with dilute hydrochloric acid. Other analyses which are sometimes submitted, but not generally required, are forms of sulfur and paste pH. Presently, numerous methods and variations on methods are in use for weatherization (leaching) tests. Because of the variety of testing methods available, it is very important that the method used be described in detail (Brady and Hornberger, 1989). The documentation should include (1) the amount of water added at any time; (2) the amount of water withdrawn at any time; (3) the amount of sample being leached; (4) the particle size(s) of the sample; (5) chemical analysis of the water used in the leaching test; (6) the frequency and duration of leaching, including flushing cycles and contact times; (7) the water level(s) relative to the position of the rock sample; (8) a description of the atmosphere in which the samples are in contact; (9) the testing temperature; (10) how and if the rock samples were composited; and (11) a sketch or photograph of the apparatus used for the testing.

Static Testing

Static testing is the laboratory analysis of geological materials for chemical characteristics such as total metal levels, pH, or total S through an analysis of the bulk concentrations in rock or soil material. Collectively, static tests as described originally in the literature have significant limitations in accurately predicting whether acidic drainage will form. Static tests were developed originally for the coal-mining industry and used later, in the late 1970s, in the metals mining industry. A commonly used version of the static test was developed by Sobek et al. (1978), and other variations (Schafer and Associates, 1987) exist as well. The static test objectives are to estimate the sulfur contents of a rock or soil sample and determine how much acid will be required to neutralize the sample. Information that is not obtained from static tests include the timing of any acid generation, if at all, acid generation, and neutralization reaction rates or effluent water quality. Static testing originally assumed that all the sulfur reported occurs as pyrite, that all the pyrite present is completely oxidized to sulfate and ferric hydroxide, that any hydrogen ions produced are neutralized by the calcium carbonate, and that all reactions are instantaneous. Static tests are most useful when the acid generation behavior of a mining waste is known or has been verified by other tests.

Research has also focused on the presence of minerals that are detected by the NP analytical method, yet do not contribute to the production of alkalinity. Siderite ($FeCO_3$) has been found in mining environments, and although contributing to the measured NP, no actual neutralization has been observed in the field (Frisbee and Hossner, 1989). *Overburden sampling* is defined as sampling the geological material overlying a resource of interest, such as a coal seam or mineral deposit. In surface mining, overburden is typically removed as waste material. In an evaluation of 31 overburden samples containing siderite, pyrite, calcite, and quartz using four dissimilar methods for NP determination, siderite-containing samples showed wide variation in NP among three laboratories (Skousen et al., 1997). Using the standard Sobek et al. (1978) test for NP, Weber et al. (2004) showed that up to 432 hours may be required for complete hydrolysis of siderite-containing samples in laboratory testing, implying that inaccurate interpretations of NP are common for rock containing this siderite since routine laboratory tests would not be run for such a great length of time. The limitations of laboratory testing for NP without supporting mineralogical characterization can often lead to overestimation of NP (Lawrence and Scheske, 1997; Paktunc, 1999).

Conventional laboratory methods for determination of NP employ wet chemical methods, where the presence of carbonates in soil is made based on titration of a sample with acid followed by backtitration with a base. The mineralogical source of carbonate is not determined by the NP test. Similarly, quantification of acid-forming minerals is challenging in a laboratory setting. Analysis of total sulfur levels is accomplished routinely using standardized laboratory equipment; however, the typical Sobek method employs subsequent acid extractions to distinguish between acid-forming minerals containing sulfur and nonacid sulfur minerals. In research using pure mineral samples, Jennings and Dollhopf (1995) showed that conventional analytical methods failed to accurately characterize acid-forming minerals. Incomplete recovery of sulfur-bearing minerals has been observed using the Sobek method since a residual sulfur fraction is commonly observed in laboratory testing, implying that the standard method of dissolution failed to solubilize or dissolve the sulfide found in the sample. Regional variation is observed in the interpretation of residual sulfur, leading to nonstandardized findings. The residual sulfur component is commonly characterized as non-acid-forming organic sulfur in sedimentary rock and as acid-forming sulfide in metal mining samples.

Paste pH or Saturated Paste pH

Paste pH or saturated paste pH is the measurement of pH in a slurry of soil or rock with deionized water after allowing time for reaction of the slurry. Paste pH is a measure of the soil solution indicative of the acidity of soil water in the context of plant growth or leaching to groundwater.

Kinetic Tests

Kinetic tests are commonly run as a companion to static testing (see the description above) to measure the weathering behavior of geological material when exposed to field conditions. Kinetic tests of mine waste are typically accomplished by monitoring the chemical constituents in water resulting from simulated laboratory weathering or actual field-site weathering of mine waste materials over a period of months to years. Water is leached through the geological material and recovered as drainage. Kinetic tests may be run in a laboratory column or in the field in large containers. The quality and quantity of leachate is subsequently evaluated to offer a supporting interpretation to static testing. Six large columns each containing 1.6 tons of waste rock were evaluated over a period of three years showing two pH controls: (1) sulfide oxidation with calcite dissolution sustaining a neutral pH, and (2) simultaneous silicate and sulfide weathering occurring at an equilibrium pH of 3 to 4 (Stromberg and Banwart, 1999). During the period of investigation the columns either remained at nearly-neutral pH or became acidic after one-half

to three years of lag time. The lag time in appearance of low pH was caused by mineralogical reactions occurring in the waste rock that either neutralized the acidity formed until exhausted or rendered nonreactive, or the acid reactions required a period of time to initiate. In a companion study, Stromberg and Banwart (1999) showed that there was a large difference in weathering rates based on particle size. In the columns, particles smaller than 0.25 mm were responsible for approximately 80% of both the sulfide oxidation and silicate dissolution. Calcite particles larger than 5 to 10 mm were found to react too slowly to neutralize acid produced by sulfide oxidation. Similar unique reaction kinetics has been observed at the Bingham Canyon mine in Utah, where fresh waste rock exhibits a paste pH of 7.0. Within six years the pH of the waste rock dumps declined to 4.7, decreasing further to pH 3.7 after 50 years of weathering (Borden, 2001). Scharer et al. (2000) observed that the NP was strongly related to particle size and that particles greater than ¼ in. (6.4 mm) were only 20% consumed at the onset of acid conditions. Kinetic data on the depletion rate of NP supplemented by geochemical modeling suggests that waste rock with NP/AP ratios as high as 5 may turn acidic in the long term. This is very different from the results mentioned above by Skousen et al. (2002), who identified 2 as the ratio below which NP/AP ratios would generally not become acidic. If neutralizing minerals are depleted or nonreactive, long-term generation of acidic drainage may be initiated with potentially dire ecological consequences if untreated.

Notable uncertainty exists in the long-term predictions of acid generation from geological materials found in mining environments. Evaluation of environmental impact statements from 25 mines performed by Kuipers et al. (2006) showed that 15 of 25 mines (60%) exceeded surface water quality standards for metals and pH after permitting.

Humidity Cells

Humidity cells are pieces of laboratory equipment used to simulate the weathering of rock in a small benchtop enclosure where soil or rock is wetted and dried repeatedly over a period of months to years to monitor changes in drainage water quality. A humidity cell is used in a specialized type of kinetic testing. Similarly, kinetic tests performed using humidity cells over a three- to seven-year period showed that rates of acid generation have a 50% chance of stabilizing within one year, while the remainder of the humidity cells fluctuated significantly throughout the test periods (Morin and Hutt, 2000).

Assessment of Acid Rock Drainage and Metals Release

Canada's Mine Environment Neutral Drainage (MEND) program was implemented to develop and apply new technologies to prevent and control acid drainage. Recognizing acid drainage as the greatest environmental problem facing the mining industry, and the regulatory agencies' responsibility to protect the environment and safeguard human health, the MEND program was funded jointly by Natural Resources Canada and the Mining Association of Canada. In 2005, MEND released a report (Price, 2005), whose purpose was to improve the assessment and mitigation of metal leaching/acid rock drainage (ML/ARD). It achieves this goal by providing a comprehensive list of information and data necessary to assess the potential for ML/ARD, and multiple strategies for mitigation. The document is intended to be used as a general guide for the mining industry, regulators, environmental advocacy groups, and other stakeholders. The MEND program uses the term *acid rock drainage* to describe the acidic water drainage from mines.

The MEND report (Price, 2005) recommends a set of informational variables and data that should be generated and developed so that informed decisions can be made with respect to the potential for acid drainage and toxic metal release. These recommendations were intended to mitigate the consequences of

sulfide mineral oxidation caused by mining, milling, and other processes involved in metal resource development. These information requirements are summarized below.

General Site Characteristics

These include location, access, climate, ecology, history of previous mining, waste materials, geology, hydrology, mineralogy, descriptions of all materials that will be excavated or exposed, soils, reclamation objectives, end land uses, data tables, relevant figures, and other pertinent information. This is not exhaustive, and site-specific information and data will be required.

Specific Material Characterization and Predictions of ML/ARD

The ability to accurately predict the potential for ML/ARD requires a careful and complete characterization of all materials and waste types under the probable weathering conditions (i.e., oxygen, bacteria, moisture, volumes of materials, etc.). Representativeness and adequacy of samples collected, measures of variability and uncertainty, and analytical procedures selected need to be appropriate. Industry-regulatory quality assurance and quality control procedures must be followed. To be complete, predictions and assessments are to be made before mining (baseline data), during the operational phase, following mining, and long term. The document defines specific tests used to define the geological and mineralogical properties of materials.

Static and Kinetic Tests

Static tests require appropriate sampling intensity, sample preparation, determinations of elemental concentrations (total and water soluble), and full acid–base accounting. Kinetic tests are recommended to evaluate reaction rates and to predict and measure drainage chemistry. Humidity cell, column, and actual field verification testing should be conducted. Monitoring of site drainage (i.e., seeps, mine drainage, pit lakes, etc.) should include parameters to be evaluated and the frequency of monitoring during and following mining.

Assessment of Waste Materials

Waste materials may include waste rock, tailings, treatment wastes, low-grade ore, and overburden materials. All media require assessments and predictions for acid drainage and release of metals and postdisposal weathering of waste piles, including changes in pH, carbonate content, and soluble weathering products (acid water and metals). Thermal properties, pore gas composition, and oxygen concentrations may be significant parameters in assessments of long-term water quality degradation.

The MEND document (Price, 2005) also provides an approach to interpretation and display of the characterization data. Identification of ARD-generating materials is important, but toxicity from metals with neutral pH can be a significant factor and is not to be overlooked. Predicting drainage chemistry is based on data and information gathered and their proper interpretation. Factors include the weathering environment and climate, data predicting the ARD/ML potential, anticipated rates of leaching from mine wastes and mine workings, metal releases based on kinetic tests, and geochemical modeling. Additional issues relate to stream alkalinity, dilution, and natural attenuation.

Estimating environmental and ecological impacts should be based on identifying potential receptors, endangered species, sensitivity and distributions of selected species, and forms of exposure. A conceptual site model can be useful in determining mechanisms of contaminant release, contaminant pathways, and receptors of concern. Acute and chronic toxicity testing of identified aquatic and terrestrial receptors, and

pre- and postmining monitoring programs are recommended.

In the United States, the National Research Council (1999) took up the issue of metal mining, recognizing the controversy associated with permitting and compliance in hardrock mining. The committee was well versed as to the potential deleterious impacts of mining and spent most of their deliberative time contemplating the weaknesses in the existing regulatory framework. Recommendations were put forward for federal agency consideration of suggestions regarding greater coordination and use of the best available scientific practices. This report did not explore technical topics such as acid mine drainage in detail; rather, the recommendations were policy-oriented.

Water Quality and Acid Mine Drainage: Premine Predictions and Postmine Comparisons

An integrated acid mine drainage research program (Maest et al., 2005; Kuipers et al., 2006) was conducted comparing predicted and actual water quality at dozens of hardrock mine sites in the United States. Both studies were enormous in scope and environmental importance and were researched and peer-reviewed extensively prior to being published. The overall purpose of the research was to examine the reliability of water quality predictions prior to hardrock mining operations. The approach included reviewing the history and accuracy of water quality predictions in environmental impact statements (EISs) for major hardrock mines and then examining and comparing actual water quality to the predictions postulated in the EISs. A total of 183 mines were identified. The investigation focused on 25 mines as case studies for in-depth analysis. Nearly all of the EISs reviewed reported that they expected acceptable water quality (concentrations lower than relevant standards) after mitigation was taken into account. Data analyses in this report, in general, refuted these EIS predictions. Major findings of the investigation are presented below.

Surface Water

The majority of the case study mines exceeded surface water quality standards, due to mining-related activities. The specific water quality parameters exceeding standards varied between sites and were not specifically identified in the report.

Groundwater

The majority of the case study mines also exceeded drinking water standards in groundwater. In terms of postmitigation groundwater quality impacts, the majority of the mines that predicted low groundwater quality impacts in their EISs were above the water quality standards. Most mines predicted no impacts on groundwater quality after mitigation was in place, but in the majority of case study mines, impacts have occurred.

Metals of Concern

In the majority of the mine cases, the elements that most often exceeded standards or that had increasing concentrations in groundwater or surface water included toxic heavy metals such as copper, cadmium, lead, mercury, nickel, or zinc, arsenic and sulfate, and cyanide.

Acid Mine Drainage

The majority of the case study mines predicted a low potential for acid drainage in one or more EISs. Of

the 25 case study mines, 9 (36%) mines have developed acid drainage on site as of the date of the study. Of these 9 mines, 8 (89%) predicted low acid drainage potential initially or had no information on acid drainage potential. Nearly all the mines that developed acid drainage either underestimated or ignored the potential for acid drainage in their EISs.

Factors Leading to Failures in Predicting Postmine Water Quality and Acid Mine Drainage

In comparing predicted and actual water quality at hardrock mines (Kuipers et al., 2006), it was noted that failures are usually associated with poor hydrological and geochemical characterization. The first area of failure relates to insufficient or inaccurate hydrological characterization, and the associated overestimations of dilution, lack of hydrogeological understanding, overestimations of discharge volumes, and underestimations of storm size. The second area of failure was insufficient or inaccurate geochemical characterization of the proposed mine resulting from not collecting adequate and representative geochemical samples for analysis.

Treatment of Acid Mine Drainage

Water treatment for elevated metal levels and acidity is a common outcome of acid mine drainage. The effectiveness and feasibility of water treatment is highly variable, depending on the treatment methods employed and unique site characteristics. Water treatment installations may include both passive and active systems. Passive water treatment systems, typically wetlands, operate without chemical amendments and without motorized or mechanized assistance. In contrast, active water treatment systems are highly engineered water treatment facilities commonly employing chemical amendment of acid mine water to achieve a water quality standard specified in a discharge permit. In-depth evaluation of acid mine drainage treatment options was not performed as part of this literature review; rather, emphasis was placed on prevention of acid mine drainage formation. Active treatment systems are operational at the Berkeley pit, Butte, Montana; Britannia Beach, British Columbia; Iron Mountain mine, Shasta County, California; and Idaho Springs/Clear Creek, Colorado. Passive treatment systems are most frequently employed in Appalachian coal-mining regions for control of acidic drainage. Semipassive treatment systems are also in use where alkaline amendments are added to surface water at remote sites such as the Summitville Superfund site in Colorado.

Recommendations for Acidic Drainage Minimization

Acidic drainage from mines is observed at many mine sites, and the undesirable consequences of acidification are well documented. Every effort should be made to minimize the causes of acid generation. Because mineralogy and other factors (particle size, reactivity of NP, and presence of oxidizers) that influence acid mine drainage formation are highly variable from one mine to another, and among different geological materials within a proposed mine site, accurate prediction of future acid generation based on current research, models, and understanding is difficult and costly. In addition, concern has arisen over the lag time between waste emplacement and observation of an acid drainage problem. Where there is acid generation, there is no general method to predict its long-term duration or to predict when acidic drainage will begin. There are historical and, now, modern mining examples of long-term acid mine drainage generation requiring active treatment in perpetuity. There are two primary approaches to addressing acid mine drainage: (1) circumvent mining sulfide-rich ore deposits with high acid mine drainage potential, and (2) implementing mitigation measures to limit potential acid mine drainage impacts. It is noted that avoiding mining of sulfide ores with the potential to form acid mine drainage may be difficult because they are most often associated with the mineral resource of interest.

Selective handling and avoidance of sulfide ore and overburden is a strategy for minimizing the risk of future acid generation (Skousen et al., 1998). In a review of selective handling of acid-forming materials in coal mining in the eastern United States, Perry et al. (1997) found that selective handling had not eliminated acid formation, due in part to the inherent difficulty in segregating benign overburden from acid-forming waste. In some mining operations, acid-forming minerals can be avoided through the mine planning process or through using underground mining rather than surface mining.

Mine waste isolation and avoidance of oxidizing conditions can be achieved using several methods that keep sulfides isolated from oxygen. Subaqueous disposal of tailings and waste rock below the water table is commonly practiced in Canada as a protocol for mine reclamation (Samad and Yanful, 2004). Constructed wetlands are also commonly used (Skousen et al., 1998). Paste backfill is a mining methodology for the minimization of acid formation by backfilling mine workings using a mixture of mine tailings, portland cement, and other binders to create a waste disposal option that is both geotechnically stable and geochemically nonreactive since sufficient NP can be added to neutralize any future acidity (Benzaazoua and Bussiere, 2002). Depyritization of tailings can be accomplished to remove sulfide minerals from waste products to create a benign sand fraction suitable to use as a general backfill and a companion low-volume sulfide concentrate requiring careful disposal. Most mine tailings contain small amounts of sulfide minerals that can readily be separated from non-acid-forming silicate minerals using conventional mineral processing equipment to create a cleaned material with sufficient NP to ameliorate any future acidity (Benzaazoua et al., 2000).

In many cases, the measures described above are most effective when used in combination and adapted to the situation at a specific site. For the most part, only limited data are available to document the long-term effectiveness of any of these controls. The report by Kuipers et al. (2006) provides a unique and well-documented view of the failure to predict the formation of acid mine drainage at many hardrock mines. Many research investigations are being conducted by university, government, and industrial entities to develop new treatment strategies for acid mine drainage. The transfer of laboratory data to site-specific conditions (i.e., climate, geology, physical properties of ores, etc.) can be problematic and significantly affect their feasibility and performance in the field.

Thorough baseline studies of the biological, hydrological, and geochemical conditions characteristic of a unique site are required to provide a basis for long-term monitoring and provide an insight into mechanistic processes involved in acid mine drainage evolution (Edwards et al., 2000). Associated financial assurances for resource mitigation in the event of default of a mine property are also required (National Research Council, 1999) to ensure both short- and long-term mitigation of acid mine drainage and the associated impacts on water quality, wildlife, and the environment.

Based on a review of the acid mine drainage literature, it is clear that accurate prediction of the onset and aggressiveness of low-quality acidic water discharge is perilously difficult using the best science available. Multiple complex geochemical, biological, and hydrological factors create a daunting task for mining engineers to recover mineral resources profitably while preventing the discharge of metals and acidity to surface water and groundwater. The historical practices of the mining industry make it clear that serious and significant efforts must be made to minimize environmental damage due to acid generation.

Summary

Acid mine drainage commonly forms as a result of natural geochemical processes that oxidize metal sulfides exposed at the Earth's surface by mining. The acid drainage is almost always begun by an aerobic microbial process in the presence of oxygen, and once started the sulfide oxidation processes will

proceed with little likelihood that prevention of the continuing sulfuric acid generation can occur without significant effort. Burying active acid sulfate soils or coal mine stockpiles where acid mine drainage has already started will probably not stop the sulfide oxidation. For new mine or construction projects, prevention must relate to proper surface project design; keeping surface water and oxygen away from sulfide-rich sediments; keeping soils and rocks inundated with water having little or no dissolved oxygen, high organic carbon, or other reducing agents; and monitoring carefully so that if acid drainage begins, other engineering controls and designs can be implemented early. Unfortunately, most countries in which hardrock or coal mining has occurred historically suffer from existing conditions that are likely to have already caused the acid drainage process to begin. In these situations, with orphan sites where no responsible parties are available for cleanup and where governments and environmental agencies do not have adequate remedial funding or regulatory authority, acid drainage challenges are enormous and the resulting acid drainage can threaten groundwater, surface water, wildlife, and the environment.

Oxidation of sulfur and hydrolysis of iron result in acid sulfate waters which have been observed at thousands of historic mine sites and at operational mines where mitigation measures have failed to prevent the release of acid mine drainage to downgradient surface waters. Resulting low-pH conditions mobilize metals from mine waste materials, resulting in degradation of surface water and groundwater quality, impairing the physical, chemical, and biological environment. Based on historical and current standards, premine prediction and the characterization of the risk of acid mine drainage formation are frequently inaccurate and estimated to be low, leading to notable water quality degradation and environmental damage when the mines are later developed.

In sum, the mining industry has spent significant financial resources to predict, prevent, mitigate, control, and stop the release of acid mine drainage using the best available technologies. However, acid mine drainage remains one the greatest environmental liabilities associated with coal and metals mining, especially in pristine environments with economically and ecologically valuable natural resources. Evidence to date from current literature and field observations suggests that permitting large-scale surface mining in sulfide-hosted rock is likely to produce degradation of surface water, groundwater, and/or the environment. Future scientific and engineering opportunities for addressing and preventing acid generation at coal and hardrock mines are created by these environmental challenges to resource extraction.

Problems and Questions

1. Explain the natural geochemical processes that oxidize metal sulfides exposed at Earth's surface.
2. How do low-pH conditions mobilize metals from waste materials, resulting in degradation of water quality?
3. How do the challenges of controlling acid generation potential in sulfide-hosted rock create future opportunities for creative scientists and engineers?
4. Can static tests determine the timing of acid generation?
5. Explain the differences of scale between bench scale or laboratory testing and field testing.
6. What hydrogeological features would it be appropriate to evaluate in a bench test?

References and Suggested Reading

Agricola, G., 1556. De Re Metallica. Translated in 1912 by H.C. Hoover and L.H. Hoover. Republished by Dover, New York, 1950, 572 pp.

Baldigo, B.P., and Lawrence, G.B., 2000. Composition of fish communities in relation to stream acidification and habitat in the Neversink River, New York. Transactions of the American Fisheries Society, vol. 129, no. 1, pp. 60–76.

Barry, K.L., Grout, J.A., Levings, C.D., Nidle, B.H., and Piercey, G.E., 2000. Impacts of acid mine drainage on juvenile salmonids in an estuary near Britannia Beach in Howe Sound British Columbia. Canadian Journal of Fisheries and Aquatic Sciences, vol. 57, no. 10, pp. 2031–2043.

Beltman, D.J., Clements, W.H., Lipton, J., and Cacela, D., 1999. Benthic invertebrate metals exposure, accumulation, and community level effects downstream from a hard rock mine site. Environmental Toxicology and Chemistry, vol. 18, no. 2, pp. 299–307.

Benzaazoua, B., and Bussiere, B., 2002. Chemical factors that influence the performance of mine sulphidic paste backfill. Cement and Concrete Research, vol. 32, no. 7, pp. 1133–1144.

Benzaazoua, B., Bussiere, B., Kongolo, M., McLaughlin, J., and Marion, P., 2000. Environmental desulphurization of four Canadian mine tailings using froth flotation. International Journal of Mineral Processing, vol. 60, no. 1, pp. 57–74.

Borden, R., 2001. Geochemical evolution of sulfide-bearing waste rock soils at the Bingham Canyon mine, Utah. Geochemistry: Exploration, Environment, and Analysis, vol. 1, no. 1, pp. 15–21.

Boudou, A., Maury-Brachet, R., Coquery, M., Durrieu, G., and Cossa, D., 2005. Synergic effect of gold mining and damming on mercury contamination in fish. Environmental Science and Technology, vol. 39, no. 8, pp. 2448–2454.

Brady, K.B.C., and Hornberger, R.J., 1989. Mine drainage prediction and overburden analysis in Pennsylvania. In: Abstracts, Annual West Virginia Surface Mine Drainage Task Force Symposium, April 25–26, Morgantown, WV.

Brady, K.B.C., Smith, M.W., and Schueck, J., 1998. Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania. Pennsylvania Department of Environmental Protection, Harrisburg, PA.

Center for Streamside Studies, 2002. Environmental Impacts of Hardrock Mining in Eastern Washington. College of Forest Resources and Ocean and Fishery Sciences, University of Washington, Seattle, WA.

Cooper, E.L., and Wagner, C.C., 1973. The effects of acid mine drainage on fish populations. In: Fish and Food Organisms in Acid Waters of Pennsylvania. EPA-R#-73-032. U.S. Environmental Protection Agency, Washington, DC, 114 pp.

Edwards, K.J., Bond, P.L., Druschell, G.K., McGuire, M.M., Hamers, R.J., and Banfield, J.F., 2000. Geochemical and biological aspects of sulfide mineral dissolution: lessons from Iron Mountain, California. Chemical Geology, vol. 169, no. 3–4, pp. 383–397.

Farag, A.M., Skaar, D., Nimick, D.A., MacConnell, E., and Hogstrand, C., 2003. Characterizing aquatic health using salmonids mortality, physiology, and biomass estimates in streams with elevated concentrations of arsenic, cadmium, copper, lead, and zinc in the Boulder River watershed, Montana. Transactions of the American Fisheries Society, vol. 132, no. 3, pp. 450–457.

Frisbee, N.M., and Hossner, L.R., 1989. Weathering of siderite ($FeCO_3$) from lignite overburden. In: Proceedings of the Symposium on Reclamation: A Global Perspective, Calgary, AB, Canada.

Fromm, P.O., 1980. A review of some physiological and toxicological responses of freshwater fish to acid stress. Environmental Biology of Fishes, vol. 5, no. 1, pp. 79–93.

Griffith, M.B., Lazorchak, J.M., and Herlihy, A.T., 2004. Relationships among exceedances of metals criteria, the results of ambient bioassays, and community metrics in mining impacted streams. Environmental Toxicology and Chemistry, vol. 23, no. 7, pp. 1786–1795.

Hansen, J.A., Woodward, D.F., Little, E.E., DeLonay, A.J., and Bergman, H.L., 1999. Behavioral avoidance: possible mechanism for explaining abundance and distribution of trout in a metals-impacted river. Environmental Toxicology and Chemistry, vol. 18, no. 2, pp. 313–317.

Hansen, J.A., Welsh, P.G., Lipton, J., and Cacela, D., 2002. Effects of copper exposure on growth and survival of juvenile bull trout. Transactions of the American Fisheries Society, vol. 131, no. 4, pp. 690–697.

Hill, R.D., 1974. Mining impacts on trout habitat. In: Proceedings of a Symposium on Trout Habitat, Research, and Management. Appalachian Consortium Press, Boone, NC.

Howells, G.D., Brown, D.J.A., and Sadler, K., 1983. Effects of acidity, calcium, and aluminum on fish survival and productivity: a review. Journal of the Science of Food and Agriculture, vol. 34, no. 6, pp. 559–570.

Jennings, S.R., and Dollhopf, D.J., 1995. Acid–base account effectiveness for determination of mine waste potential acidity. Journal of Hazardous Materials, vol. 41, pp. 161–175.

Jennings, S.R., Dollhopf, J.D., and Inskeep, W.P., 2000. Acid production from sulfide minerals using hydrogen peroxide weathering. Applied Geochemistry, vol. 15, pp. 235–243.

Jennings, S.R., Neuman, D.R., and Blicker, P.S., 2008. Acid Mine Drainage and Effects on Fish Health and Ecology: A Review. Reclamation Research Group Publication, Bozeman, MT, 29 pp.

Johnson, D.W., Simonin, H.A., Colquhoun, J.R., and Flack, F.M., 1987. In situ toxicity tests of fishes in acid waters. Biogeochemistry, vol. 3, no. 1–3, pp. 181–208.

Kaeser, A.J., and Sharpe, W.E., 2001. The influence of acidic runoff episodes on slimy sculpin reproduction in Stone Run. Transactions of the American Fisheries Society, vol. 130, no. 6, pp. 1106–1115.

Kimmel, W.G., 1983. The impact of acid mine drainage on the stream ecosystem. In: Pennsylvania Coal: Resources, Technology, and Utilization. S.K. Majumdar and E.W. Willard, eds. Pennsylvania Academy of Science, Bradford, PA, pp. 424–437.

Kuipers, J.R., Maest, A.S., MacHardy, K.A., and Lawson, G., 2006. Comparison of Predicted and Actual Water Quality at Hardrock Mines: The Reliability of Predictions in Environmental Impact Statements. Kuipers & Associates, Butte, MT, 228 pp.

Lawrence, R.W., and Scheske, M., 1997. A method to calculate the neutralization potential of mining wastes. Environmental Geology, vol. 32, no. 2, pp. 100–106.

Maest, A., Kuipers, J., Travers, C., and Atkins, D., 2005. Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties, and State-of-the-Art. Kuipers & Associates, Butte, MT, 90 pp.

Maret, T.R., and MacCoy, D.E., 2002. Fish assemblages and environmental variables associated with hard-rock mining in the Coeur d'Alene River Basin, Idaho. Transactions of the American Fisheries Society, vol. 131, no. 5, pp. 865–884.

Martin, A.J., and Goldblatt, R., 2007. Speciation, behavior, and bioavailability of copper downstream of a mine-impacted lake. Environmental Toxicology and Chemistry, vol. 26, no. 12, pp. 2594–2603.

McGuire, M.M., Edwards, K.J., Banfield, J.F., and Hamers, R.J., 2001. Kinetics, surface chemistry, and structural evolution of microbially mediated sulfide dissolution. Geochimica et Cosmochimica Acta, vol. 65, no. 8, pp. 1243–1258.

Menendez, R., 1978. Effects of acid water on Shavers Fork: a case history. In: Surface Mining and Fish/Wildlife Needs in the Eastern United States. FWS/OBS 78–81. U.S. Department of the Interior, Fish and Wildlife Service, Washington, DC, pp. 160–169.

Morin, K.A., and Hutt, N.M., 2000. Lessons learned from long-term and large-batch humidity cells. In: 5th International Conference on Acid Rock Drainage, Denver, CO., Society for Mining, Metallurgy and Exploration, Englewood, CO.

Munshower, F.F., Neuman, D.R., Jennings, S.R., and Phillips, G.R., 1997. Effects of Land Reclamation Techniques on Runoff Water Quality from the Clark Fork River Floodplain, Montana. U.S. EPA, Office of Research and Development, Washington, DC, pp. 199–208.

National Research Council, 1999. Hardrock Mining on Federal Lands. National Academies Press, Washington, DC.

Nordstrom, D.K., and Alpers, C.N., 1999. Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. Proceedings of the National Academy of Sciences USA, vol. 96, no. 7, pp. 3455–3462.

Nordstrom, D.K., and Southam, G., 1997. Geomicrobiology: interactions between microbes and minerals. Mineral Society of America, vol. 35, pp. 261–390.

Nordstrom, D.K., Jenne, E.A., and Averett, R.C., 1977. Heavy Metal Discharges into Shasta Lake and Keswick Reservoir on the Sacramento River, California: A Reconnaissance During Low Flow. USGS Open-File Report 76–49. U.S. Geological Survey. Reston, VA.

Paktunc, A.D., 1999. Mineralogical constraints on the determination of neutralization potential and prediction of acid mine drainage. Environmental Geology, vol. 39, no. 2, pp. 103–112.

Perry, E.F., Gardner, M.D., and Evans, R.S., 1997. Effect of acid material handling and disposal on coal mine drainage quality. In: 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada.

Price, W.A., 2005. List of Potential Information Requirements in Metal Leaching/Acid Rock Drainage Assessment and Mitigation Work. MEND Report 5.10E, Canada Centre for Mineral and Energy Technology, Ottawa, ON, Canada.

Samad, M.A., and Yanful, E.K., 2005. A design approach for selection the optimum water cover depth for subaqueous disposal of sulfide mine tailings. http://pubs.nrc-cnrc.gc.ca/rp/rppdf/t04-094.pdf.

Schafer and Associates and Reclamation Research, 1987. Laboratory Analytical Protocol for the Streambank Tailings and Revegetation Study, Silver Bow Creek, RI:FS, EPA Region VIII. Document SBC-STARS-LAP-F-RI-121187.

Scharer, J.M., Bolduc, L., Pettit, C.M., and Halbert, B.E., 2000. Limitations of acid–base accounting for predicting acid rock drainage. In: 5th International Conference on Acid Rock Drainage, Denver, CO. Society for Mining, Metallurgy and Exploration, Englewood, CA.

Schmidt, T.S., Soucek, D.J., and Cherry, D.S., 2002. Modification of an ecotoxicological rating to bioassess small acid mine drainage-impacted watersheds exclusive of benthic macroinvertebrate analysis. Environmental Toxicology and Chemistry, vol. 21, no. 5, pp. 1091–1097.

Sherlock, E.J., Lawrence, R.W., and Poulin, R., 1995. On the neutralization of acid rock drainage by carbonate and silicate minerals. Environmental Geology, vol. 25, no. 1, pp. 43–54.

Skousen, J.G., and Ziemkiewicz, P.F., 1996. Acid Mine Drainage Control and Treatment, 2nd ed. West Virginia University and the National Mine Land Reclamation Center, Morgantown, WV.

Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Dohen, L., and Ziemkiewicz, P., 1997. Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, vol. 26, no. 3, pp. 673–681.

Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., and Hellier, W., 1998. Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage Acid Technology Initiative (ADTI). http://www.ott.wrcc.osmre.gov/library/hbmanual/hbtechavoid/hbtechavoid.pdf.

Skousen, J., Simmons, J., McDonald, L.M., and Ziemkiewicz, P., 2002. Acid–base accounting to predict post-mining drainage quality on surface mines. Journal of Environmental Quality, vol. 31, pp. 2034–2044.

Smith, R.M., Grube, W.E., Arkle, T., and Sobek, A., 1974. Mine Spoil Potentials for Soil and Water Quality. EPA-670/2-74-070. U.S. EPA, Cincinanati, OH, 303 pp.

Sobek, A., Schuller, W., Freeman, J.R., and Smith, R.M., 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoils. EPA-600/2-78-054. U.S. EPA, Cincinnati, OH, 203 pp.

Soucek, D.J., Cherry, D.S., Currie, R.J., Latimer, H.A., and Trent, G.C., 2000. Laboratory and field validation in an integrative assessment of an acid mine drainage-impacted watershed. Environmental Toxicology and Chemistry, vol. 19, no. 4, pp. 1036–1043.

Stromberg, B., and Banwart, S., 1999. Weathering kinetics of waste rock from the Aitik copper mine, Sweden: scale dependent rate factors and pH controls in large column experiments. Journal of Contaminant Hydrology, vol. 39, no. 1–2, pp. 59–89.

United Nations Environmental Programme, 2000. Cyanide Spill at Baia Mare Romania, UNEP/OCHA Assessment Mission; Spill of Liquid and Suspended Waste at the Aurul S.A. Retreatment Plant in Baia Mare, Geneva. UNEP, and Office for the Co-Ordination of Humanitarian Affairs, Ocha Assessment Mission, Romania, Hungary, Federal Republic of Yugoslavia.

United Nations Environment Programme, 2002. Chronology of Major Tailing Dam Failures. UNEP, Division of Technology, Industry and Economics. http://www.mineralresourcesforum.org/incidents/index.htm.

U.S. Department of Agriculture, 1993. Acid Mine Drainage from Impact of Hard Rock Mining on the National Forests: A Management Challenge. Program Aid 1505. USDA Forest Service, Washington, DC, 12 pp.

U.S. Environmental Protection Agency, 1995. Human Health and Environmental Damages from Mining and Mineral Processing Wastes. U.S. EPA, Office of Solid Waste, Washington, DC.

Warner, R.W., 1971. Distribution of biota in a stream polluted by acid mine drainage. Ohio Journal of Science, vol. 71, no. 4, pp. 202–215.

Weber, P.A., Thomas, J.E., Skinner, W.M., and Smart, R.C., 2004. Improved acid neutralization capacity assessment of iron carbonates by titration and theoretical calculation. Applied Geochemistry, vol. 19, no. 5, pp. 687–694.

Woodward, D.F., Goldstein, J.K., Farag, A.M., and Brunbaugh, W.G., 1997. Cutthroat trout avoidance of metals and conditions characteristic of a mining waste site: Coeur d'Alene River, Idaho. Transactions of the American Fisheries Society, vol. 126, no. 4, pp. 699–706.

Younger, P.L., Banwart, S.A., and Hedin, R.S., 2002. Mine Water: Hydrology, Pollution, Remediation. Springer-Verlag, New York.

19
Acid–Base Accounting Associated with Acid Rock Drainage

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This chapter is primarily a detailed description of acid–base accounting (ABA) concepts commonly used in the mining industry. ABA is used as a screening method to quickly determine the amount of neutralizing agent that is needed for acid-generating materials such as pyrite-rich rocks, sediments, and soils. Although the text refers to acid rock drainage (ARD), the concepts are also applicable to acid mine drainage (AMD) and acid sulfate soils.

Introduction

Acid–base accounting (ABA) is a screening procedure whereby the acid-neutralizing potential (assets) and acid-generating potential (liabilities) of rock samples are determined, and the difference, the net neutralizing potential (equity), is calculated. The net neutralizing potential and/or the ratio of neutralizing potential to acid-generation potential is compared with a predetermined value, or set of values, to divide samples into categories that either require, or do not require, further determinative acid potential generation test work. Just as different methods of accounting, such as cash or accrual basis, will present different sets of books to an auditor, so different methods of conducting ABA test work will generate different sets of sample data for evaluation. Rules and guidelines have been developed by mine regulatory and permitting agencies (e.g., Steffen, Robertson and Kirsten, 1992; Brady et al., 1994; Miller, 1995; Price and Errington, 1998) for ABA procedures that may be likened to the rules and guidelines of financial accounting.

In its most basic form, ABA is simply a screening process. It provides no information on the speed (or kinetic rate) with which acid generation or neutralization will proceed, and because of this limitation, the test work procedures used in ABA are referred to as *static procedures*. However, the evaluation of ABA data in conjunction with mineralogical and petrological data can, for certain ABA procedures, give a degree of neutralization rate prediction to ABA.

The potential for a given rock to generate and neutralize acid is determined by its mineralogical composition. This includes not only the quantitative mineralogical composition, but also individual mineral grain size, shape, texture, and spatial relationship with other mineral grains. The term *potential* is used because even the most detailed mineralogical analysis, when combined with ABA, can give only a worst-case value for *potential* acid production, and depending on the neutralization potential procedure used, worst case, most likely case, and best case values for *potential* neutralization capability. The field generation and neutralization of ARD represents the degree to which these *potential* values are realized in practice.

Neutralization Potential Procedures

Because of the complexity and difficulty of translating detailed mineralogical data into neutralization potential (NP) values (see Lawrence and Sheske, 1997; Paktunc, 1998a,b,c) for the large number of samples evaluated in a typical ABA screening program, chemical procedures have been developed as a

substitute for mineralogical procedures. However, to maximize the information obtained from chemical procedures in ARD prediction, they should always be used in combination with determinative mineralogical methods.

These chemical procedures are generically termed *neutralization potential determination methods* or *procedures*. The most common such procedures are:

- Lapakko neutralization potential test procedure
- BC Research Inc. (BCRI) initial test procedure
- Modified acid–base accounting procedure for neutralizing potential (Lawrence)
- Peroxide siderite correction for the Sobek method (Skousen et al.)
- Sobek neutralization potential method

Despite individual procedural differences, these methods all involve:

- Reaction of a sample with a mineral acid of measured quantity
- Determination of the base equivalency of the acid consumed
- Conversion of measured quantities to a neutralizing potential in g/kg or kg/metric ton (mt) or mt/1000 mt calcium carbonate ($CaCO_3$)

Note that the last step is an accounting convenience—a sample with no calcium carbonate content or even any carbonate content may nevertheless produce a neutralizing potential value that is recorded as g/kg or kg/mt $CaCO_3$. The methods determine the quantity of the sample that is dissolved by the prescribed quantity of acid for the sample and procedure used.

The procedures listed above differ primarily in the degree of aggressiveness of acid reaction with the sample (i.e., the variety of minerals attacked by acid and the degree of mineral dissolution). Table 19.1 summarizes the procedural conditions described and suggests, qualitatively, which minerals are dissolved by each procedure.

Table 19.1 Procedural Conditions for Neutralization Potential Determination

Procedure	Acid	Amount of Acid Added	End pH of Acid Addition	Test Duration	Test Temperature	Minerals Dissolved
Lapakko	Sulfuric	To reach pH 6.0	6.0	Up to 1 week	Ambient	Ca + Mg carbonates
BCRI initial	Sulfuric	To reach pH 3.5	3.5	16–24 h[a]	Ambient	Ca + Mg carbonates Possibly chlorite,[b] limonite[c]
Modified Sobek	Hydrochloric	Determined by fizz test	2.0–2.5	24 h	Ambient	Ca + Mg carbonates Some Fe carbonate, biotite, chlorite, amphibole[d] Olivine (forsterite-fayallite)
Sobek	Hydrochloric	Determined by fizz test	0.8–2.5[e]	Until gas evolution ceases (test	Elevated (ca. 90°C)	Mineral carbonates Ca-feldspar, pyroxene, olivine (forsterite-fayallite)[f,g] Some

				including titration up to 3 h)		feldspars (anorthoclase > orthoclase > albite); ferromagnesians: pyroxene, hornblende, augite, biotite[a]
Sobek–siderite correction	Procedure as for Sobek, but with peroxide correction for siderite					Ca + Mg carbonates, excludes Fe + Mn carbonates; otherwise, as per Sobek
Net carbonate value	Method uses combustion-infrared analysis, not acid digestion					Calcite, dolomite, ankerite, siderite
Inorganic carbon–carbonate[h]	Method uses Leco furnace or equivalent, not acid digestion					Mineral carbonates

[a]Downing and Madeisky (1997).

[b]Warren (1996).

[c]Mills (1997).

[d]Kwong and Ferguson (1997).

[e]Lawrence and Wang (1997); actual pH extremes were pH 0.35 to 5.2.

[f]Lapakko (1994).

[g]BHP Diamonds, Inc. (1995a,b, 1996).

[h]It is common practice to determine inorganic (mineral) carbonate for samples subject to NP determination for comparison with NP measured.

Notes:

1. The chemical formula for the chlorite group of minerals is $A_{5–6}Z_4O_{10}(OH)_8$, where A = Al, Fe^{2+}, Fe^{3+}, Li, Mg, Mn^{2+}, Ni and Z = Al, B, Fe^{3+}, Si, while that for biotite is $K(Mg,Fe^{2+})_3(Al,Fe^{3+})Si_3O_{10}(OH,F)_2$ (Fleischer, 1981). Note that both contain the (OH) group. The general chemical formula for the feldspar group of minerals is XZ_4O_8, where X = Ba, Ca, K, Na, NH_4, Sr and Z = Al, B, Si (Fleischer, 1981). Note the absence of the (OH) group.

2. Although NP is reported as kg $CaCO_3$/mt or mt $CaCO_3$/1000 mt, the carbonate minerals that contribute to NP include calcite, dolomite [$(Ca,Mg)CO_3$], magnesite ($MgCO_3$), ankerite [$Ca(Fe^{2+},Mg,Mn)(CO_3)_2$], siderite ($FeCO_3$), and rhodochrosite ($MnCO_3$). However, the Fe and Mn components of carbonates hydrolyze to generate hydrogen ions and therefore have no net neutralizing power (Skousen et al., 1997). Carbonate NP values must be reduced to account for Fe and Mn carbonates if such carbonates are present in the sample.

3. The low-pH endpoint for the Sobek method is significant, since Morin et al. (1995) in their international kinetic database of 396 kinetic tests from 60 mines show that pH fell below a value of pH 2 for only one test (see also Chapter 20).

4. Very few data have been published on mineral reactivity during NP determination by any of the procedures noted above.

Lawrence and Wang (1996) analyzed the leachate from samples tested using the Sobek and modified Sobek procedures for aluminum and other cations contained in aluminosilicates. From the higher cation concentrations in the leachate found using the Sobek method, the authors concluded that the Sobek method dissolved more silicate minerals than did the modified Sobek method.

Downing (1996) compared the quantities of various elements dissolved (mg/kg) for waste rock samples tested by the BCRI initial and Sobek methods. For the five samples tested, the Sobek method dissolved more aluminum than did the BCRI initial method by factors of 1.5, 8.2, 11.2, 12.4, and 3.9 to 1. Again, this clearly demonstrates increased dissolution of aluminosilicate minerals by the Sobek method over the

BCRI initial method.

Mills (1997) analyzed leachate from eight waste rock samples tested using the BCRI initial method for a number of cations, including aluminum and potassium. Enhanced levels of aluminum and potassium (for all samples) in the leachate were taken as evidence of the dissolution of potassium aluminosilicates.

Kwong and Ferguson (1997) studied 26 samples treated using the modified Sobek method and variations, and utilized x-ray diffraction to determine mineralogical changes. They concluded that biotite, chlorite, and amphibole contributed to the NP determined, whereas quartz, muscovite, plagioclase, and K-feldspar did not.

In general, NP determined by the various methods increases with the degree of aggressiveness of the method in the order NP-sobek > NP-modified Sobek > NP-BCRI initial > NP-Lapakko. In addition, for the Sobek and modified Sobek methods, an overestimation of the fizz test rating will generally yield a higher NP value because of the action of the additional acid. The fizz test is examined later in the chapter.

While the role of carbonate minerals in ARD neutralization has been well established, that of aluminosilicate minerals has not. Sherlock et al. (1995) and Downing and Madeisky (1997) have discussed the behavior of aluminosilicate minerals in the neutralization process from a theoretical viewpoint and commented on the practical implications. Downing and Madeisky (1997) have proposed the use of a lithogeochemistry-derived pair of net buffering capacity indices: a short-term index based on carbonate content and a long-term index based on calcium plus potassium content. The role of iron manganese carbonates is discussed by Frostad et al. (2003).

Lawrence and Wang (1997) have suggested the relationship between mineral reactivity and method of NP determination shown in Table 19.2. Such relationships are not inconsistent with the comparisons made earlier. Table 19.3 is another table of reactivity of neutralizing minerals (at pH 5) that has been widely quoted (e.g., Kwong, 1993a,b). Although these values for relative reactivity are given for pH 5 rather than the lower pH values used for most NP determination procedures, they are generally consistent with our previous discussion (although the categorization of garnet as fast weathering seems inappropriate). Kwong (1993a) has suggested that all of the minerals in the dissolving, fast weathering, and intermediate weathering groups (relative reactivity 1.0, 0.6, and 0.4, respectively) be considered as having practical neutralizing capability in the field.

Table 19.2 Relationship Between Mineral Reactivity and NP Determination Method

Relative Mineral Reactivity	**Neutralizing Mineral**	**Extent of Reaction by NP Method**
More reactive	Carbonates	Carbonate
Less reactive	Ca-feldspar, olivine	Modified Sobek
	Pyroxenes, amphiboles	Sobek
	Sorosilicates, phyllosilicates	
	Plagioclase feldspar	
	K-feldspar	
	Quartz	

Table 19.3 Relative Mineral Reactivity

Mineral Group	Typical Minerals	Relative Reactivity at pH 5
Dissolving	Calcite, aragonite, dolomite, magnesite, brucite	1.0
Fast weathering	Anorthite, nepheline, olivine,[a] garnet, jadeite, leucite, spodumene, diopside, wollastonite	0.6
Intermediate weathering	Epidote, zoisite, enstatite,[b] hypersthene, augite, hedenbergite, hornblende, glaucophane, tremolite, actinolite, anthophyllite, serpentine, chrysotile, talc, chlorite, biotite	0.4
Slow weathering	Albite, oligoclase, labradorite, montmorillonite, vermiculite, gibbsite, kaolinite	0.02
Very slow weathering	K-feldspars, muscovite	0.01
Inert	Quartz, rutile, zircon	0.004

Source: After Sverdrup (1990) and Kwong (1993a,b).

[a]See Schott and Berner (1983, 1985), Grandstaff (1980), Hutchison and Ellison (1992), Banfield et al. (1991), Loughnan (1969), and Luce et al. (1972).

[b]See Grandstaff (1977).

That aluminosilicate minerals are dissolved to some extent by ARD, and therefore act as neutralizing agents, is shown clearly by aluminum analyses of ARD from established sites. Figure 19.1 shows some of the 1995 monitoring data for the 2200-level adit discharge at the former Britannia mine in British Columbia. It can be seen that aluminum analyses range from about 35 to 65 mg/L, with an ARD pH of about 3, indicating significant dissolution of aluminosilicate minerals. In this case the use of an NP determination method that considers only carbonates as a source of neutralizing capacity would probably underestimate the true, or field, neutralizing capacity.

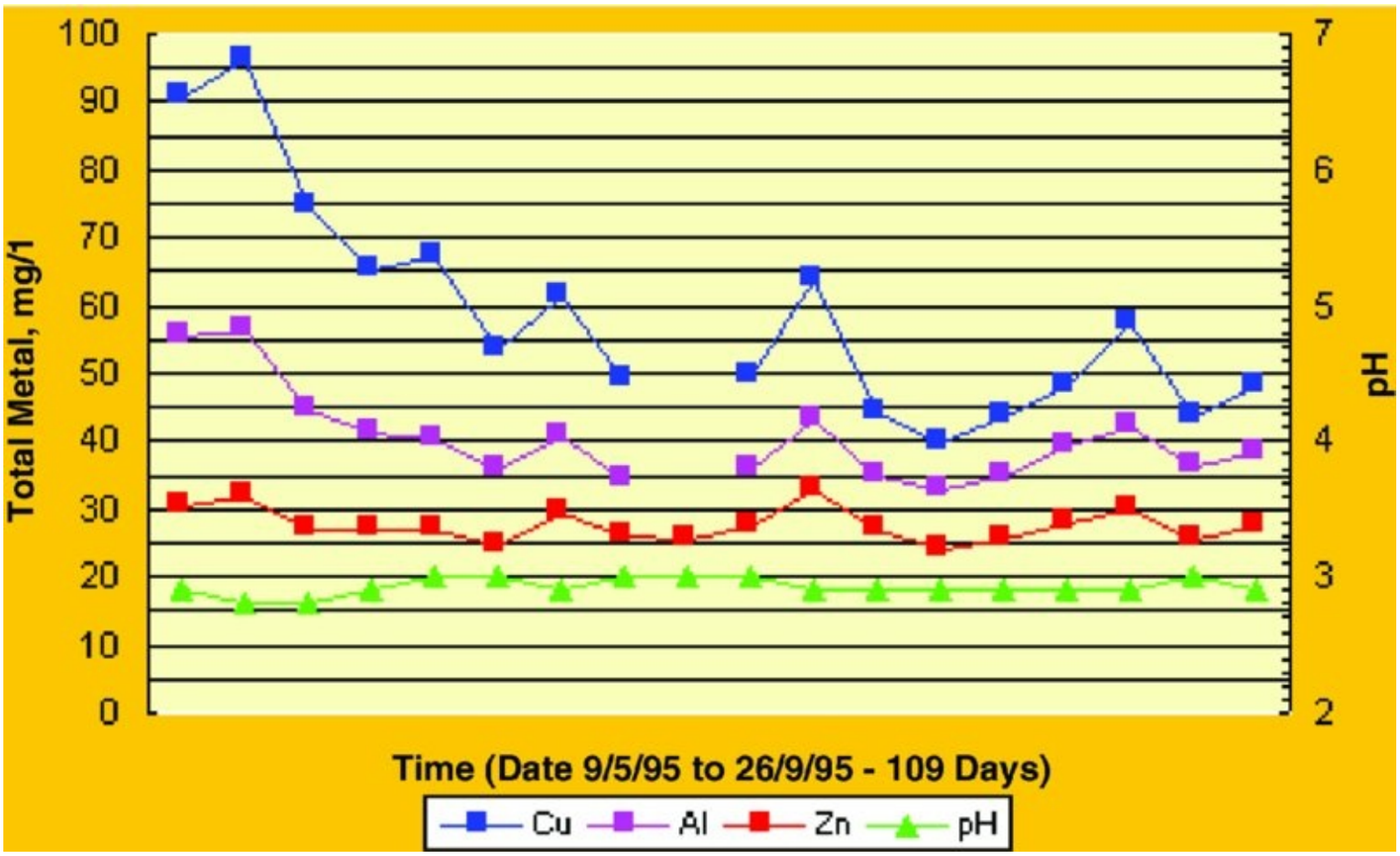

FIGURE 19.1 Metal concentration monitoring data, 2200-level adit, Britannia mine, BC, 1995. (From Gordon Ford, BC Ministry of Environment.)

Blowes et al. (1992) have reported elevated concentrations of both silica and aluminum in tailings water, as have Alpers and Nordstrom (1990) for waste rock drainage. Alpers and Nordstrom (1990) also concluded, based on computer speciation modeling, that at Iron Mountain, California, the minerals albite, chlorite, sericite, epidote, and calcite contributed to ARD neutralization. Morin et al. (1988) reported that tailings water migrating from the uranium tailings impoundments studied was saturated with respect to aluminum and silica.

Downing and Madeisky (1997) measured the NP of four low-carbonate samples as a function of time using the BCRI initial method (the standard BCRI initial method typically takes 16–24 h). For comparison, they conducted similar tests with the Canadian Reference Material for Standard Acid–Base Accounting, NBM-1, which is carbonate bearing. Their results for the four low-calcite samples and for the standard are shown in Figures 19.2 and 19.3.

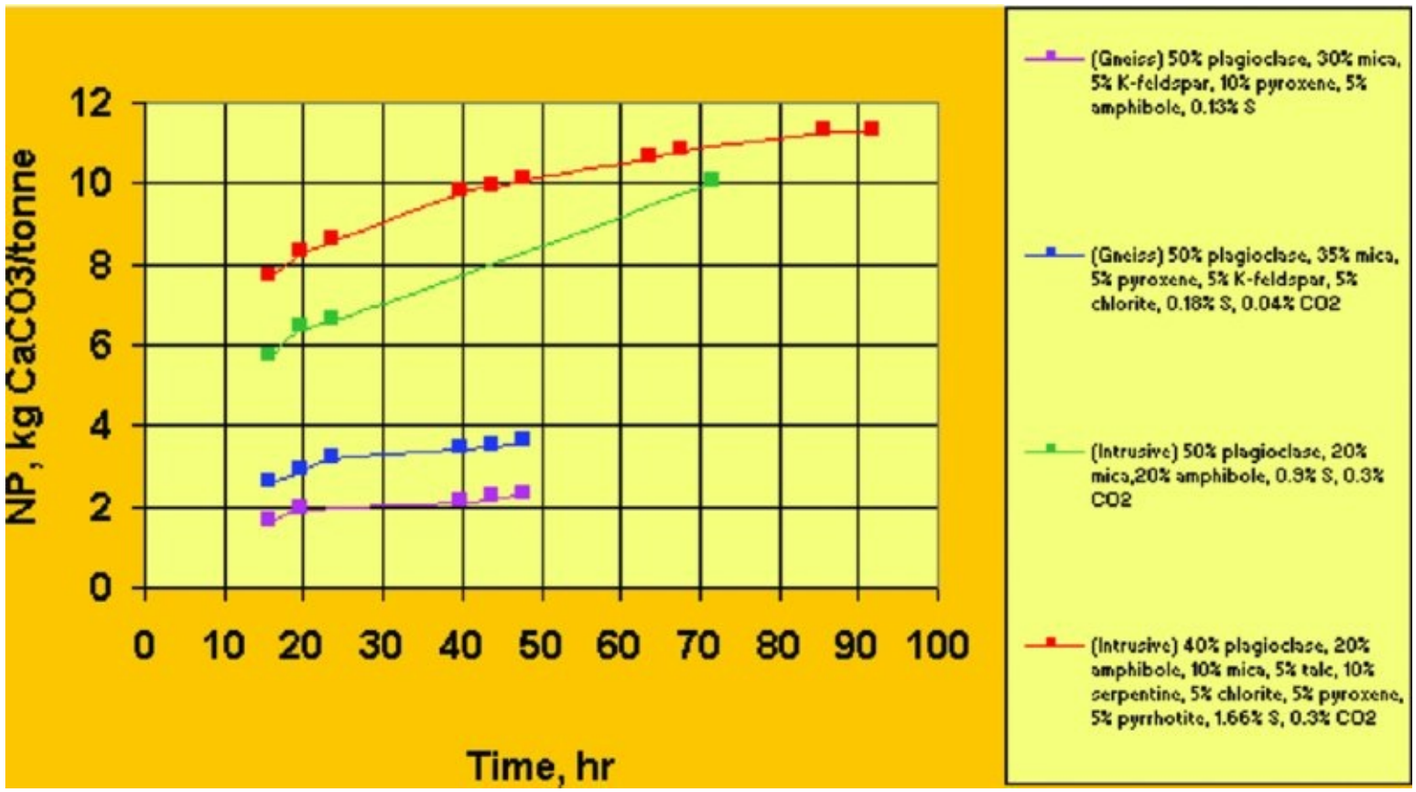

FIGURE 19.2 NP versus time (BCRI initial method) for four low-carbonate samples. (From Downing and Madeisky, 1997.)

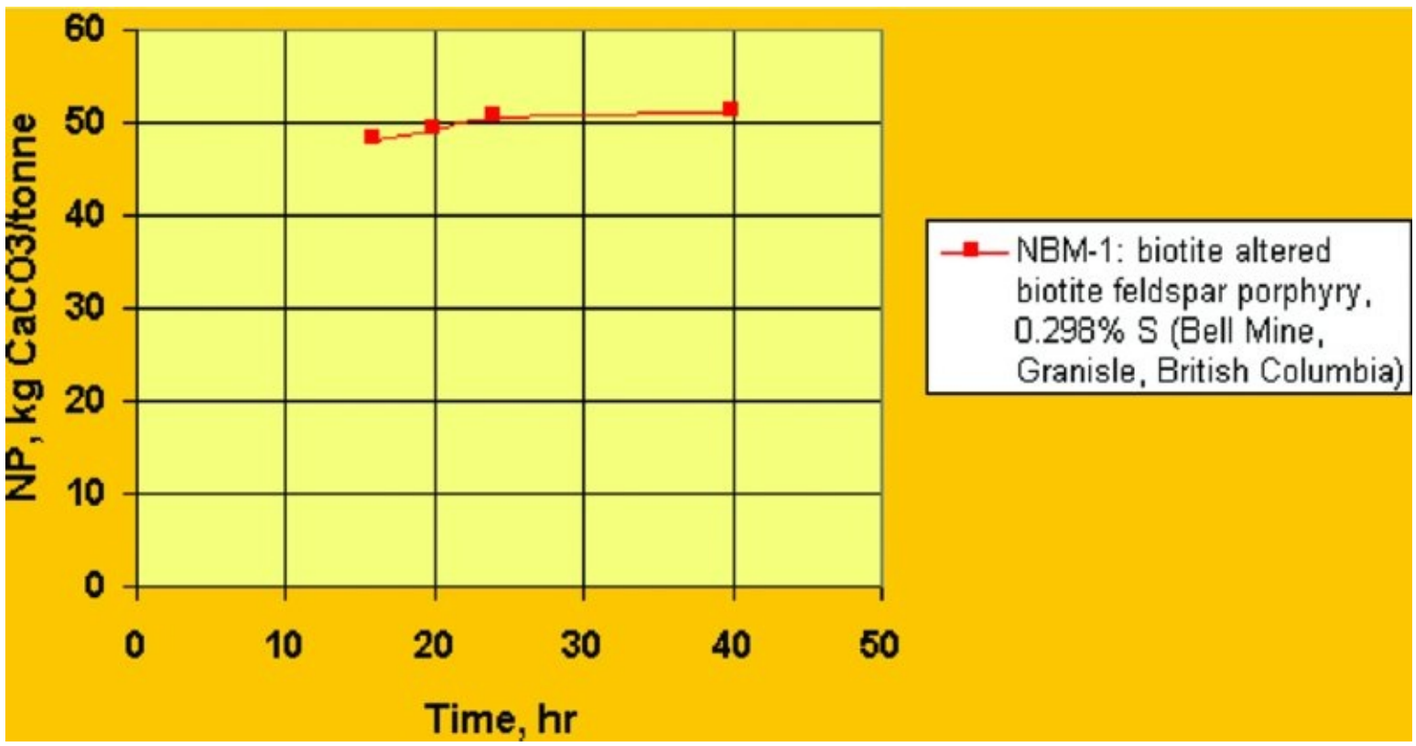

FIGURE 19.3 NP versus Time (BCRI initial method) for Canadian reference material for standard acid–base accounting, NBM-1. (From Downing and Madeisky, 1997.)

These data tend to indicate that where carbonate is the predominant neutralizing species (i.e., the NBM-1 standard), the BCRI initial method gives an NP value that does not increase with time after the normal test duration (16 to 24 h), whereas the slower reaction rates of noncarbonate neutralizing minerals give NP

values that are time dependent. The degree of time dependency appears to be a function of mineralogical composition, as would be expected from earlier discussion. Further, it seems likely that the NP for the four low-carbonate samples is contributed by mica, chlorite, pyroxene, and amphibole.

It should be clear from the discussion above that no single NP determination method will give the true, or field, NP for any given sample. As a very broad generalization, it may be said that for a sample containing carbonates and reactive silicates:

1. The Lapakko and inorganic carbon–carbonate methods will tend to give a worst-case neutralization potential, since the carbonates are credited but other minerals are not.
2. The Sobek method will tend to give a best-case neutralizing potential since all carbonates and other minerals soluble at the lowest pH of the test will be credited.
3. The BCRI initial and modified Sobek methods will tend to give a most-likely-case neutralization potential, since the carbonates and only the most reactive silicates are credited.

The statements above notwithstanding, it should be understood that even the Lapakko and inorganic carbon–carbonate methods may overestimate the real, or field, neutralizing potential of materials. This is possible because some of the neutralizing minerals present may be inaccessible to ARD because of physical placement or entrainment, or because of "armoring" by metal precipitates (Hyman et al., 1996).

Fizz Test (Sobek Method)

The fizz test used in the Sobek and modified Sobek methods to determine the quantity of acid used in the digestion is subjective, in that it requires a judgment by the test operator. Lawrence and Wang (1997), Skousen et al. (1997), and Soregaroli and Lawrence (1997) have compared different laboratory assessments of the fizz rating and examined the effects of such differences on the NP measured. Lawrence and Wang (1997) evaluated 112 samples of waste rock and tailings and eight certified reference standards (concentrates, ores, and metallurgical) to determine the effect of the fizz rating on NP by the Sobek method. Table 19.4 shows the typical end pH and range of end pH obtained in test work for the four fizz ratings: none, slight, moderate, and strong.

Table 19.4 pH Endpoints for Various Fizz Ratings Using the Sobek NP Procedure

Fizz Rating	Typical End pH	pH Range
No fizz	2.0–2.5	1.6–5.2
Slight fizz	1.5	0.76–2.1
Moderate fizz	1.0	0.77–1.83
Strong fizz	0.8	0.35–1.07

Source: Lawrence and Wang (1997).

NP values (Sobek method) reported for three samples using a strong Fizz rating exceeded those obtained with a slight Fizz rating by 527, 400, and 337%. The authors have reported this work in detail (Lawrence and Wang, 1996). In their "Experimental Objectives and Methods" section, the authors state: "To compare NP value variations in the Sobek procedure when different fizz ratings were used for each waste sample tested. This was done since the assigning of a fizz rating can be subjective. In addition, some test laboratories, for convenience, do not carry out a fizz test in strict accordance with the Sobek procedure. Instead, acid additions are made according to a strong fizz rating." Lawrence and Sheske (1997) and Lawrence and Wang (1996) provide more information on the determination of NP.

Soregaroli and Lawrence (1997) considered four Dublin Gulch waste rock samples with fizz ratings of moderate, weak, moderate, and weak by Chemex Laboratories and strong, strong, strong, and strong by University of British Columbia (UBC) laboratories. The NP values determined (Sobek method) by the UBC laboratories for their (strong) fizz ratings exceeded those by Chemex for their (moderate and weak) ratings by 586, 417, 686, and 223%.

Skousen et al. (1997) examined 31 samples of overburden from coal mines in Pennsylvania and West Virginia, using three independent laboratories. All three laboratories assigned the same fizz rating to 16 of the samples, of which 11 were from the "Si group" of 17 samples containing mostly quartz and clays and little or no carbonates (calcite and siderite). There was no agreement for the "Fe group" (6 samples containing 18 to 65% siderite and little or no calcite), complete agreement for the "Ca group" (3 samples containing 23 to 90% calcite and no siderite), and some agreement, 2 of 5, for the "S group" (5 samples containing 1 to 63% pyrite).

Where there were differences in fizz ratings, they were generally by one category; two samples gave a two-category range and one a three-category range. The authors compared NP values determined using the reported fizz ratings with NP values obtained using the next-higher fizz rating. They concluded:

> The NP values were higher for all Fe group samples and variable for the other groups when using more acid. It is evident that NP results for samples containing siderite are more sensitive to the assigned fizz rating than samples without siderite. For example, sample Si14, a gray shale shale devoid of siderite, showed little variation in NP (7 to 8 mg/1000 mg) when the fizz rating was increased from 1 to 2, while the NP values for sample Fe5, containing 18% siderite, increased from 64 to 234 mg/1000 mg when the fizz rating was increased from 2 to 3. When greater amounts of acid were used during sample digestion, most samples yielded a higher NP value.

The authors suggest an alternative procedure to the fizz test to determine the carbonate content of rocks and report experimental testing of the alternative procedure on 26 of the 31 samples examined previously.

It is clear from the discussion above that the subjectivity of the fizz test used in the Sobek method may, depending on the sample, produce widely differing NP values for a single sample. It is also likely that consistent use of a strong rating rather than a determined rating may lead to unusually high NP values that may be misleading. Finally, it would be useful to see the effects of fizz rating on NP values determined by the modified Sobek method.

Acid Generation Potential Procedures

The determination of acid generation potential is less fraught with difficulties than is the neutralization potential. When no organic material containing sulfur is present in samples, the potential for acid generation is attributed to the potential oxidation of sulfide minerals to sulfate (sulfuric acid). Sulfide minerals include the common iron minerals pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$), and metallic sulfides such as chalcopyrite ($CuFeS_2$), sphalerite (ZnS), and galena (PbS). The sulfide sulfur content is taken to react stoichiometrically with oxygen and water to form sulfuric acid, which has an equivalence in calcium carbonate, and hence acid generation potential in kg $CaCO_3$/mt or mt $CaCO_3$/1000 mt is calculated.

Samples may also contain sulfate minerals such as gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), and barite ($BaSO_4$) (previously oxidized samples may also contain a wide range of sulfate-containing oxidation products, such as melanterite ($FeSO_4 \cdot 7H_2O$), brochantite [$Cu_4(SO_4)(OH)_6$], jarosite [$KFe_3(SO_4)_2(OH)_6$], and alunite [$KAl_3(SO_4)_2\ (OH)_6$]. Sulfate minerals have no potential to oxidize to sulfuric acid, although

some oxidation products, such as melanterite, may dissolve, hydrolyze, and generate acidity. (This is generally of more concern in kinetic tests such as humidity cells than in static tests.)

Where sulfate mineral content is very much less than sulfide mineral content (and in the absence of organic sulfur), sulfide sulfur may be approximated to total sulfur. Whether acid generation potential may be calculated satisfactorily from total sulfur instead of sulfide sulfur will, therefore, depend on sample sulfate mineral content and will be site-specific. Unless total sulfur analysis is used, it is necessary to conduct additional analytical procedures in order to determine sulfide sulfur.

Sobek et al. (1978) describe analytical procedures to determine total sulfur, sulfide sulfur, acid-leachable sulfate sulfur, acid-insoluble sulfate sulfur, and organic sulfur. Acid-leachable sulfate sulfur includes gypsum and anhydrite, and acid-insoluble sulfate sulfur includes barite. The necessity of determining all of these sulfur components for any give suite of samples is rare. For example, for western Canadian metalliferous mines, it is common practice to determine sulfide sulfur as the difference between total sulfur by a Leco furnace and acid-soluble sulfate sulfur. The occasional necessity to correct for barite can be determined from barium assays obtained from whole-rock analyses. Acid generation potential is calculated from sulfide sulfur content. It is infrequently acknowledged that each analytical stage added to the sulfide sulfur determination introduces an additional analytical error, and that these errors are cumulative.

All mines in British Columbia are currently subject to the *ARD Guidelines for Mine Sites in British Columbia* (Price and Errington, 1998). These guidelines, encourage a site-specific philosophy for potential ARD prediction.

> ‘The recommended procedure for determining the maximum potential for future mineral acid generation is to calculate it using the sulfide-S content measured using an expanded sulfur speciation analysis. Complete sulfur speciation may not be required if there are no organic-S or sulfate-S components present, however, these assumption should be verified. As many base metal deposits contain significant sulfate-S, the use of total-S as a sulfide-S measure may result in a large over-estimation of AP.

According to Hyman et al. (1996) and Brady (1997), current Appalachian practice for coal mine overburden samples favors acid generation potential (termed *maximum potential acidity*) from total sulfur determined by a Leco furnace. The regulatory process does not prohibit the use of expanded sulfur forms analysis, but the use of total sulfur is considered more reliable (Brady, 1990). For further discussion of this subject, see Day (1991).

Screening Assessment Criteria

After the neutralizing potential and acid generation potential have been determined for a sample, it is necessary to combine these two values in a manner that allows comparison with set criteria based on experience or regulation. The two methods of combination commonly used are:

- The difference in value between NP and AP, or the net neutralization potential (NNP = NP − AP)
- The ratio of NP value to AP value, or the neutralization potential ratio (NPR = NP/AP)

The former is the preference for Appalachian coal mines; the latter, for western Canadian metalliferous mines.

From earlier discussion of NP and AP determination methods, it should be clear that an NNP or NPR

value for a sample will reflect the method used to determine NP and AP, but will be affected particularly by the method used for NP determination. Since potentially large ranges of values for NP can, depending on the procedures used, be obtained for a single sample, it follows that both NNP and NPR are also sensitive to procedures. This has, in the past, resulted in the reporting of a myriad of subclasses of NP, AP, NNP, and NPR that are all procedure-specific, and has resulted in considerable confusion among practitioners of ARD (or AMD) prediction. These reporting problems have occurred less in Appalachian coal mining, where the Sobek NP and total sulfur MPA have been used fairly consistently, than in North American metalliferous mining. It is partly to ensure consistency of reporting that the British Columbia guidelines recommend Sobek NP and sulfide sulfur AP [but see the earlier section on the the fizz test (the Sobek method)].

For 39 Pennsylvania coal mine sites where historical data have been maintained, it has been reported that material with an NNP (Sobek NP − MPA) greater than 15 mt $CaCO_3$/1000 mt had alkaline drainage. For 78% of the same sites, material with an NNP less than or equal to zero had acidic drainage (Brady et al., 1994). For these sites the “gray zone,” or range of NNP for which prediction is difficult, is represented by material with an NNP greater than zero but less than 15 mt $CaCO_3$/1000 mt. Brady has commented (Brady, 1997) that the siderite modification of the Sobek method (Skousen et al., 1997) may reduce the range of the gray zone. Other NNP criteria have been proposed and discussed by Smith et al. (1974, 1976), the Surface Mine Drainage Task Force (1979), Skousen et al. (1987), di Pretoro and Rauch (1988), the British Columbia Acid Mine Drainage Task Force (1989), Ferguson and Morin (1991), Patterson and Ferguson (1994), and Perry and Brady (1995).

Paste pH has been considered as an assessment criterion by Smith et al. (1974, 1976), the Surface Mine Drainage Task Force (1979), and Miller and Murray (1988), and percent total sulfur as an assessment criterion by Miller and Murray (1988) and Brady and Hornberger (1990). NP has been considered as an assessment criterion by di Pretoro and Rauch (1988), Brady and Hornberger (1990), Brady et al. (1994), and Perry and Brady (1995).

In British Columbia, the existing guidelines (Price and Errington, 1998) state:

> The screening criteria used to evaluate a need for further test work based on acid base accounting tests are:
>
> - Materials with sulphide minerals whose net neutralizing potential (NNP = NP − AP) is negative are likely to be an acid drainage source. Exceptions are possible if the sulphide content is very low and/or there are significant slow release, noncarbonate sources of alkalinity.
> - The acid drainage potential will be considered uncertain if materials have a ratio of neutralization potential to potential acidity (NP : AP) of less than 4 : 1.

Basically, these guidelines defined a gray zone for NPR greater than 1 and less than 4. However, based on Price et al. (1997b), it is expected that the new guidelines will define two NPR gray zones (Sobek NP/sulfide sulfur AP), as shown in Table 19.5.

Table 19.5 Neutralization Potential Ratio Screening Criteria

Potential for ARD	Initial NPR Screening Criteria	Comments
Likely	<1 : 1	Possibly ARD generating
Possibly	1 : 1–2 : 1	Possibly ARD generating if NP is insufficiently reactive or is depleted at a faster rate than sulfides
Low	2 : 1–4 : 1	Not potentially ARD generating unless significant preferential exposure of sulfides along fracture planes, or extremely reactive sulfides in combination with insufficiently reactive NP
None	>4 : 1	No further ARD testing required unless materials are to be used as a source of alkalinity

Source: Price et al. (1997b).

Traditionally in British Columbia, where sample NPR values have fallen in the gray zone, kinetic test work (humidity cells or columns) has been conducted to clarify sample status with regard to acid generation potential. However, it should be possible to characterize material in the 4 < NPR > 2 zone adequately by mineralogical and petrographic test work.

A most useful method of presentation for NPR values is their plot against sulfide sulfur on logarithmic axes, as shown in Figure 19.4 for ABA data for the proposed Dublin Gulch mine in the Yukon Territory (Soregaroli and Lawrence, 1998). Figure 19.5 shows the neutralization potential ratio (NP/AP) versus sulfide sulfur for production monitoring samples of waste rock and tailings from the Colomac open-pit gold mine, which is located 221 km northwest of Yellowknife in the Northwest Territories of Canada. NPR as an assessment criterion has been discussed by di Pretoro and Rauch (1988), Cravotta et al. (1990), Ferguson and Morin (1991), Filipek et al. (1991), Ferguson and Robertson (1994), and Patterson and Ferguson (1994).

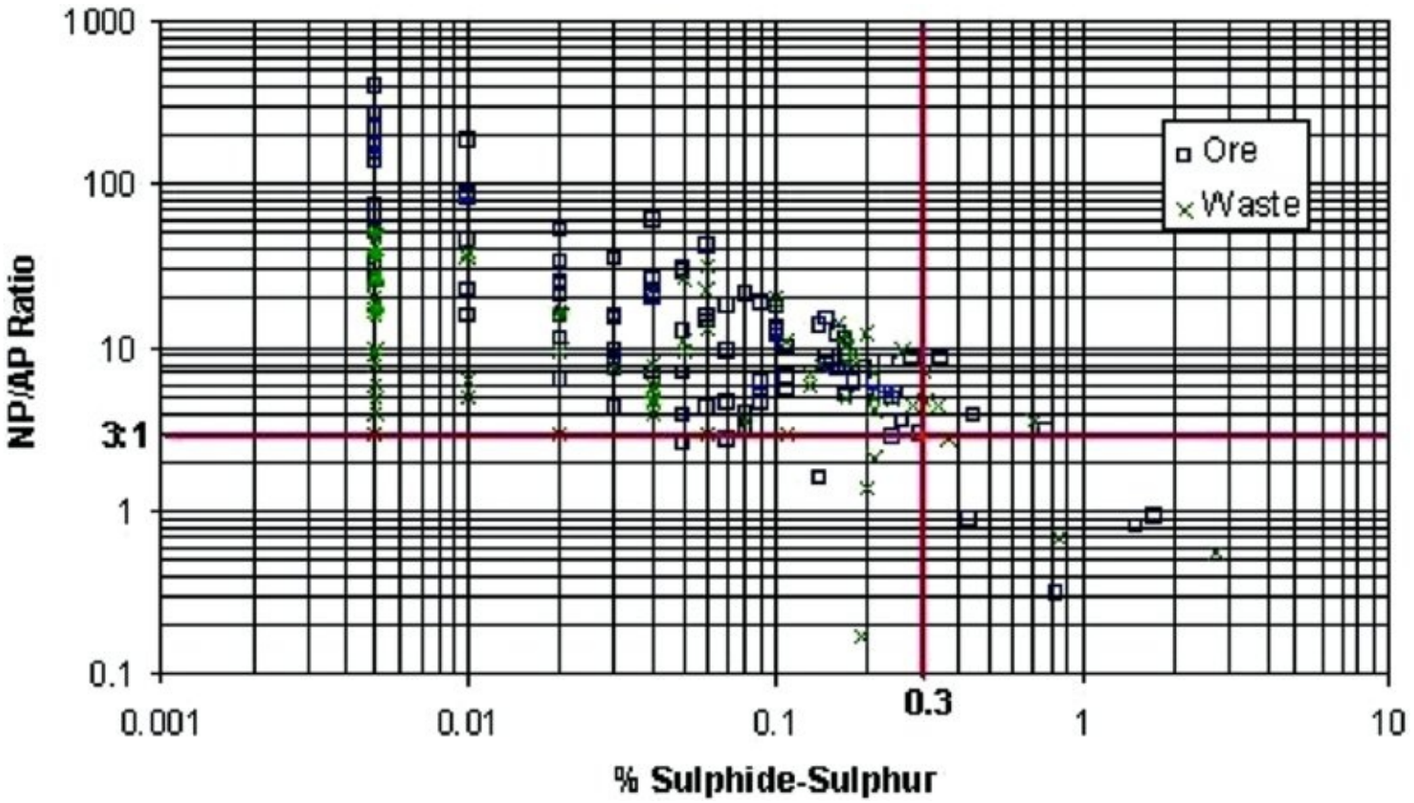

FIGURE 19.4 NPR versus sulfide sulfur for ore and waste at the proposed Dublin Gulch mine, Yukon Territory. (From Soregaroli and Lawrence, 1998.)

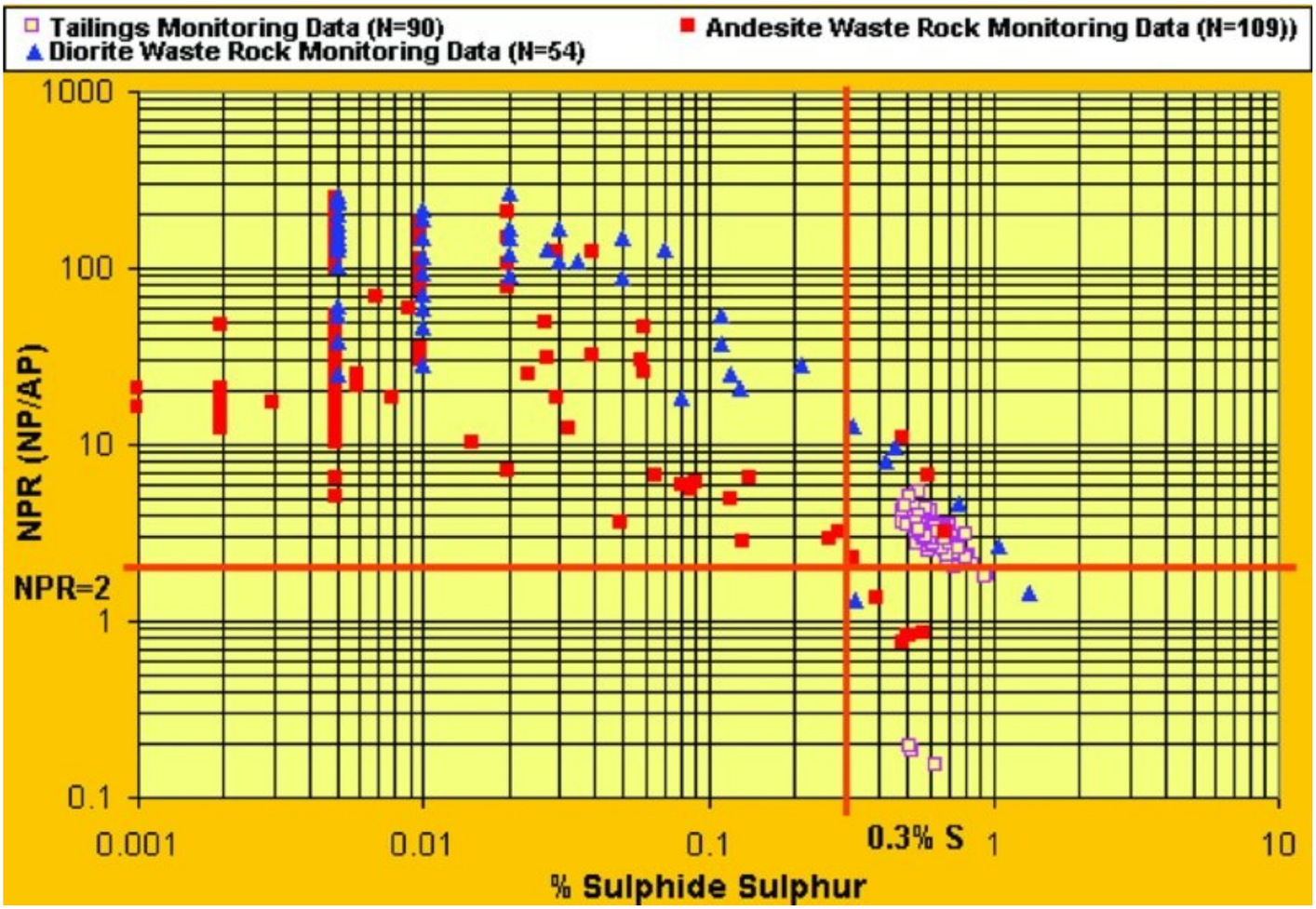

FIGURE 19.5 Neutralization potential ratio, NPR (NP/AP), versus sulfide sulfur for production monitoring samples of waste rock and tailings from the Colomac mine, Northwest Territories. (From Mills, 1998from data in Royal Oak Mines Inc., 1998.)

Acknowledgment

The basic material and concepts for this chapter were developed in part by the late Chris Mills, a mining engineer specializing in metallurgical engineering and surface chemistry. He was heavily involved as an engineer in the mining industry throughout the world for over 30 years, and as a teacher and researcher he contributed many technical papers and classes on mining and acid rock drainage. Sadly, he died unexpectedly on February 10, 1999.

References and Suggested Reading

Alpers, C.N., and Nordstrom, D.N., 1990. Stoichiometry of mineral reactions from mass balance computations of acid mine waters: Iron Mountain, California. In: Acid Mine Drainage—Designing for Closure, Geological Association of Canada–Mineralogical Association of Canada Joint Meeting, Vancouver, BC, Canada, pp. 23–33.

Banfield, J.F., Jones, B.F., and Veblen, D.R., 1991. An AEM–TEM study of weathering and diagenesis, Albert Lake, Oregon: I. Weathering reactions in the volcanics. Geochimica et Cosmochimica Acta, vol. 55, pp. 2781–2793.

BHP Diamonds, Inc., 1995a. Environmental Impact Statement: Volume I: Section 2.3.2: Petrology of the NWT Diamond Project Kimberlite Varieties and 2.25–2.28. Section 2.3.4: NWT Diamonds Project Property Geology, 2.29–2.35.

BHP Diamonds, Inc., 1995b. Waste Rock Leaching: 1995 Baseline Study Update. Yellowknife, NWT, Canada. (Contains: Morin, K.A., and Hutt, N.M., Predictions of Dissolved Concentrations in Waste Rock Drainage, Minesite Drainage Assessment Group, Vancouver, BC, Canada; Morin, K.A., and Hutt, N.M., Results of Kinetic Test Work, Minesite Drainage Assessment Group, Vancouver, BC, Canada.)

BHP Diamonds, Inc., 1996. NWT Diamonds Project: In Support of Application for Class 'A' Water Licence. Report submitted to the Northwest Territories Water Board, Yellowknife, NWT, Canada, 118 pp.

Blowes, D.W., Jambor, J.L., Appleyard, E.C., Reardon, E.J., and Cherry, J.A., 1992. Temporal observations of the geochemistry and mineralogy of a sulphide-rich mine-tailings impoundment, Heath Steele Mines, New Brunswick. Exploration and Mining Geology, vol. 1, no. 3, pp. 251–264.

Brady, K.B., 1990. Pyritic sulphur analyses for coal overburden. In: 1990 National Symposium on Mining, University of Kentucky, Lexington, KY.

Brady, K.B., 1997. Personal communication to C. Mills.

Brady, K.B., and Hornberger, R.H., 1990. The prediction of mine drainage quality in Pennsylvania. Water Pollution Control Association of Pennsylvania Magazine, vol. 23, pp. 8–15.

Brady, K.B., Perry, E.F., Beam, R.L., Bisko, D.C., Gardner, M.D., and Tarantino, J.M., 1994. Evaluation of acid–base accounting to predict the quality of drainage at surface coal mines in Pennsylvania, USA. USBM SP 06A-94. In: Proceedings of the International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA, vol. 1, pp. 138–146.

Brady, K.B., et al., 1996. Shallow groundwater flow in unmined regions of the northern Appalachian Plateau: 2. Geochemical characteristics. In: Proceedings of the 13th Annual Meeting of the American Society for Surface Mining and Reclamation, Knoxville, TN, pp. 52–61.

British Columbia Acid Mine Drainage Task Force, 1989. Draft Acid Rock Drainage Guide. BiTech Publishers, Vancouver, BC, Canada.

Cravotta, C.A., Brady, K.B., Smith, M.W., and Beam, R.L., 1990. Effectiveness of alkaline addition at surface mines in preventing or abating acid mine drainage: 1. Geochemical considerations. In: Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, West Virginia University, Morgantown, WV, vol. 1, pp. 221–226.

Day, S.J., 1991. New Methods for Determination of Key Mineral Species in Acid Generation Prediction by Acid–Base Accounting. MEND Project Report 1.16.1c. MEND, Ottawa, ON, Canada.

di Pretoro, R.S., and Rauch, H.W., 1988. Use of Acid–Base Accounts in Premining Prediction of Acid Drainage Potential: A New Approach from Northern West Virginia. Information Circular 9183. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 1–10.

Downing, B.W., 1996. Unpublished research.

Downing, B.W., and Madeisky, H.E., 1997. A lithogeochemical method for acid rock drainage prediction.

Prepared for the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, 16 pp.

Erickson, P.M., and Hedin, R., 1988. Evaluation of Overburden Analytical Methods as a Means to Predict Postmining Coal Mine Drainage Quality. Information Circular 9183. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 11–19.

Ferguson, K., and Morin, K., 1991. The prediction of acid rock drainage: lessons from the data base. In: Proceedings of the 2nd International Conference on the Abatement of Acidic Drainage, vol. 3. CANMET, Ottawa, ON, Canada, pp. 83–106.

Ferguson, K., and Robertson, J., 1994. Assessing the risk of ARD. In: International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage. Special Publication SP 06A-94. U.S. Department of the Interior, Bureau of Mines, vol. 1, pp. 2–11.

Filipek, L., Gormley, J., Ewing, R., and Ellsworth, D., 1991. Kinetic acid-prediction studies as aids to waste rock and water management during advanced exploration of a massive sulphide deposit. In: Proceedings of the 2nd International Conference on the Abatement of Acidic Drainage, vol. 3. CANMET, Ottawa, ON, Canada, pp. 191–208.

Fleischer, M., 1981. Glossary of Mineral Species 1983. Mineralogical Record, The University of Michigan, John Sampson White, 202 pp.

Frostad, S., Price, W.A., and Bent, H.G., 2003. Operational NP Determination – Accounting for Iron Manganese Carbonates and Developing a Site-Specific Fizz Rating. In: Proceedings of Sudbury 2003: Mining and the Environment Conference, Sudbury, Ontario, May 24–29.

Grandstaff, D.E., 1977. Some kinetics of bronzite ortho-pyroxene dissolution. Geochimica et Cosmochimica Acta, vol. 41, pp. 1097–1103.

Grandstaff, D.E., 1980. The dissolution rate of forsteritic olivine from Hawaiian beach sand. In: Proceedings of the 3rd International Symposium on Water–Rock Interaction, pp. 72–74.

Hutchison, I.P.G., and Ellison, R.D., 1992. Mine Waste Management: A Resource for Mining Industry Professionals, Regulators and Consulting Engineers. CRC Press/Lewis Publishers, Boca Raton, FL, pp. 127–184.

Hyman, D.M., Hawkins, J.W., Kleinmann, R.L.P., and Watzlaf, G.R., 1996. The art and science of mine drainage prediction. Unpublished manuscript, 41 pp.

Jambor, J.L., and Blowes, D.W., 1998. Theory and application of mineralogy in environmental studies of sulphide-bearing mine wastes. In: Modern Approaches to Ore and Environmental Mineralogy, L.J. Cabri, and D.J. Vaughan, eds. Mineralogical Association of Canada Short Course, vol. 27, pp. 367–402.

Kwong, Y.T.J., 1993a. Minesite acid rock drainage assessment and prevention: a new challenge for a mining geologist. In: Proceedings of the International Mining Geology Conference, Kalgoorlie, WA, pp. 213–217.

Kwong, Y.T.J., 1993b. Prediction and Prevention of Acid Rock Drainage from a Geological and Mineralogical Perspective. MEND Report 1.32.1, NHRI Contribution CS-92054. MEND, Ottawa, ON, Canada.

Kwong, Y.T.J., and Ferguson, K.D., 1997. Mineralogical changes during NP determinations and their

implications. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 435–447.

Lapakko, K.A., 1994. Determinations for metal mine waste and a proposed alternative. In: Proceedings of the International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage, Pittsburgh, PA. Special Publication SP 06A-94. U.S. Department of the Interior, Bureau of Mines, Washington, DC, vol. 1, pp. 129–137.

Lawrence, R.W., and Sheske, M., 1997. A method to calculate the neutralization potential of mining wastes. Environmental Geology, vol. 32, pp. 100–106.

Lawrence, R.W., and Wang, Y., 1996. Determination of Neutralization Potential for Acid Rock Drainage Prediction. MEND Report 1.16.3. MEND, Ottawa, ON, Canada, 149 pp.

Lawrence, R.W., and Wang, Y., 1997. Determination of neutralization potential in the prediction of acid rock drainage. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 449–464.

Loughnan, F.C., 1969. Chemical Weathering of the Silicate Minerals. Elsevier, New York, 154 pp.

Luce, R.W., Bartlett, R.W., and Parks, G.A., 1972. Dissolution kinetics of magnesium silicates. Geochimica et Cosmochimica Acta, vol. 36, pp. 35–50.

Miller, R.A., 1995. Mine Rock Characterization Guideline. Montana Department of Environmental Quality, Helena, MT.

Miller, S.D., and Murray, G.S., 1988. Application of acid base analysis to wastes from base metal and precious metal mines. In: Proceedings: Mine Drainage and Surface Mine Reclamation, vol. 1, Mine Water and Mine Waste. Information Circular 9183. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 29–32.

Mills, C., 1997. An Assessment of the Results of Acid Base Accounting (ABA) and Mineralogical Test Work on Eight Samples from the Proposed Minto, Yukon Territory, Minesite. Report to the Selkirk First Nation, Pelly Crossing, Yukon, 30 pp.

Mills, C., 1998. A Critical Review of Geochemical Stability, Acid Rock Drainage (ARD) and Metals Leaching Potential, and Tailings Management Aspects of the Royal Oak Mines Inc. Colomac Mine Interim Abandonment and Restoration Plan (Draft). Report to the Northwest Territories Water Board, Yellowknife, on behalf of the Dogrib Rae Band, Rae-Edzo, Northwest Territories, 20 pp.

Morin, K.A., Cherry, J.A., Dave, N.K., Lim, T.P., and Vivyurka, A.J., 1988. Migration of acidic groundwater seepage from uranium-tailings impoundments: 1. Field study and conceptual hydrogeochemical model. Journal of Contaminant Hydrology, vol. 2, pp. 271–303.

Morin, K.A., Hutt, N.M., and Ferguson, K.D., 1995. Measured rates of sulphide oxidation and acid neutralization in kinetic tests: statistical lessons from the database. In: Sudbury ’95: Mining and the Environment. CANMET, Ottawa, ON, Canada.

Paktunc, A.D., 1998a. Characterization of mine wastes for the prediction of acid mine drainage. In: Environmental Impacts of Mining Activities: Emphasis on Mitigation and Remedial Measures, J.M. Azcue, ed. Springer-Verlag, Berlin.

Paktunc, A.D., 1998b. MODAN: an interactive computer program for estimating mineral quantities based on bulk composition. Computers and Geosciences, vol. 24, no. 5, pp. 425–431.

Paktunc, A.D., 1999. Discussion of “A Method to Calculate the Neutralization Potential of Mining Wastes,” by R.W. Lawrence, and M. Sheske, Environmental Geology, vol. 38, no. 1, pp. 82–83.

Patterson, R.J., and Ferguson, K., 1994. The Gibraltar North Project assessing acid rock drainage. In: International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage. Special Publication SP 06B-94. U.S. Department of the Interior, Bureau of Mines, Washington, DC, vol. 1, pp. 12–21.

Perry, E.F., and Brady, K.B., 1995. Influence of neutralization potential on surface mine drainage quality in Pennsylvania. Presented at the West Virginia Surface Mine Drainage Task Force Symposium, April 4–5, Morgantown, WV.

Price, W.A., and Errington, J., 1998. Guidelines for Metal Leaching and Acid Rock Drainage at Minesites in British Columbia, British Columbia Ministry of Energy and Mines. p. 86.

Price, W.A., Errington, J., and Koyanagi, V., 1997a. Guidelines for the prediction of acid rock drainage and metal leaching for mines in British Columbia: I. General procedures and information requirements. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 1–14.

Price, W.A., Morin, K., and Hutt, N., 1997b. Guidelines for the prediction of acid rock drainage and metal leaching for mines in British Columbia: II. Recommended procedures for static and kinetic testing. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 15–30.

Royal Oak Mines Inc., 1998. Colomac Mine Interim Abandonment and Restoration Plan (Draft). Submission to the Northwest Territories Water Board.

Schott, J., and Berner, R.A., 1983. X-ray photoelectron study of the mechanism of iron silicate dissolution during weathering. Geochimica et Cosmochimica Acta, vol. 47, pp. 2233–2240.

Schott, J., and Berner, R.A., 1985. Dissolution mechanism of pyroxenes and olivines during weathering. In: The Chemistry of Weathering, J.I. Drever, ed. NATO ASI Series, C149, 53 pp.

Sherlock, E.J., Lawrence, R.W., and Poulin, R., 1995. On the neutralization of acid rock drainage by carbonate and silicate minerals. Environmental Geology, vol. 25, pp. 43–54.

Skousen, J. G., Sencindiver, J.C., and Smith, R.M., 1987. A Review of Procedures for Surface Mining and Reclamation in Areas with Acid-Producing Materials. West Virginia University Energy and Water Research Center, in cooperation with the West Virginia Mining and Reclamation Association and West Virginia Surface Mine Drainage Task Force, Morgantown, WV.

Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L., and Ziemkiewicz, P., 1997. Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, vol. 6, no. 3, pp. 673–681.

Smith, M.W., and Brady, K.B.C., 1990. Evaluation of acid base accounting data using computer spreadsheets. In: Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, vol. 1, J.

Skousen et al., eds. West Virginia University, Morgantown, WV, pp. 213–219.

Smith, R.M., Grube, W.E., Arkle, T., and Sobek, A., 1974. Mine Spoil Potentials for Soil and Water Quality. EPA-670/2-74-070. Prepared for U.S. Environmental Protection Agency, Cincinnati, OH.

Smith, R.M., Sobek, A., Arkle, T., Sencindiver, J.C., and Freeman, J.R., 1976. Extensive Overburden Potentials for Soil and Water Quality. EPA-600/2-76-184. Prepared for U.S. Environmental Protection Agency, Cincinnati, OH.

Sobek, A.A., Schuller, W.A., Freeman, J.R., and Smith, R.M., 1978. Field and Laboratory Methods Applicable to Overburden and Minesoils. EPA 600/2-78-054. U.S. EPA, Washington, DC, 203 pp.

Soregaroli, B.A., and Lawrence, R.W., 1997. Waste rock characterization at Dublin Gulch: a case study. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 631–645.

Soregaroli, B.A., and Lawrence, R.W., 1998. Update on waste characterization studies. Presented at the Mine Design, Operations and Closure Conference, Polson, MT, 10 pp.

Steffen, Robertson and Kirsten (BC), Inc., and BC Research and Development, 1992. Guidelines for ARD Prediction in the North. Department of Indian Affairs and Northern Development, Ottawa, ON, Canada.

Surface Mine Drainage Task Force, 1979. Suggested guidelines for methods of operation. In: Surface Mining of Areas with Potentially Acid-Producing Materials. SMDTF, Charleston, WV.

Sverdrup, H.U., 1990. The Kinetics of Base Cation Release due to Chemical Weathering. Lund University Press, Lund, Sweden, 246 pp.

Warren, J. (University of Waterloo), 1996. Personal communication to B. Downing.

20
Acid–Base Accounting Test Procedures

BRUCE W. DOWNING

This chapter is primarily a detailed description of acid–base accounting test procedures, which are used widely in the mining industry.

Introduction

Acid–base accounting (ABA) procedures have been developed from a number of sources, which are cited, and represent testing methods that have seen commercial use. A degree of editing has been used to simplify electronic publishing and to present methods in a similar format. These ABA procedures are based in part on MEND reports and documents (e.g., Coastech Research, 1989, 1991; Day, 1991; Lawrence, 1995; Lawrence and Wang, 1996), which are a primary source of hard-copy versions of many of the procedures, and there are numerous other sources (e.g., Steffen, Robertson and Kirsten, 1992). There has also been much interest in the peroxide method of siderite compensation in the Sobek procedure developed by the Pennsylvania–West Virginia Overburden Task Force.

It is current practice to calculate acid generation potential for materials in Canadian metalliferous mines from sulfide-sulfur content. This is usually accepted as the difference between total sulfur by a Leco furnace or other method, and sulfate sulfur determined chemically [for further discussion, see Day (1991) and Lawrence (1997)]. On the other hand, acid generation potential for overburden material in Appalachian coal mines is normally calculated from total sulfur using a Leco furnace.

BC Research, Inc. Initial Test (Chemical) Procedure for Evaluating Acid Production Potential of Ore and Waste Rock

Sample

The sample must be taken in such a manner that it is representative of the type of mineralization being examined. A composite consisting of a split drill core or randomly selected grab samples should be satisfactory. The number of samples to be examined will depend on the variability of the mineralization and must be left to the discretion of the geologist. The bulk sample is cone crushed to −10 mesh. A representative 250-g portion is split out, dried, and pulverized to around 60% −400 mesh for assay, the titration test, and if necessary, the confirmations test.

Assay

The pulverized sample is assayed in duplicate for total sulfur (S_{total}) in a Leco furnace or by wet chemical methods. The acid production potential of the sample, expressed as kilograms of sulfuric acid per metric ton of sample, is calculated on the basis of the total sulfur assay.

Titration Test

Duplicate l0-g portions of the pulverized sample are suspended in 100 mL of distilled water and stirred for approximately 15 min. The natural pH of the sample is recorded. The sample is then titrated to pH 3.5 with 1.0 N sulfuric acid using an automatic titrator (see Figures 20.1 and 20.2). The test is continued until less than 0.1 mL of acid is added over a 4-h period. The total volume of acid added is recorded and converted to kg/metric ton (mt) of sample.

Figure 20.1 Bank of automatic titrators for BCRI initial NP determination. (Courtesy of BC Research, Inc., Vancouver, BC, Canada.)

Figure 20.2 Pair of automatic titrators for BCRI initial NP determination. (Courtesy of BC Research, Inc., Vancouver, BC, Canada.)

For a 10-g sample, the acid consumption is given by mL 1.0 N H_2 SO_4 × 4.9 kg/mt.

Interpretation

If the acid consumption value (in kilograms of acid per metric ton of sample) exceeds the acid-producing potential (kg/mt), the sample will not be a source of acid mine drainage, and no additional work is necessary. The method described here expresses acid and neutralizing potential in kg/mt $CaCO_3$ (not H_2SO_4). If the acid consumption is less than the acid production potential or the difference is marginal, the possibility of acid mine water production exists and the confirmation test is conducted. A pH of 3.5 is chosen for titration, as above this value the acid-generating bacterium *Thiobacillus ferrooxidans* is not active.

Notes

1. It is current practice to use sulfide sulfur, not total sulfur.
2. It is current practice to express acid and neutralizing potential in kg/mt $CaCO_3$ (not H_2SO_4).

Original Reference

Bruynesteyn, A., and Duncan, D.W., 1979. Determination of acid production potnetial of waste materials. AIME Annual Meeting, New Orleans, LA, February, 19–21, paper (A-79-29), Minerals and the Environment, 1982, vol. 4, no. 1, pp. 5–8.

Test Procedures to Evaluate the Neutralization Potential of Clay (Modified B.C. Research Method)

The presence of clay in waste rock may have a latent positive contribution to NP that was not determined by the standard NP test. The following test procedure was developed after discussion with Dr. Jim Warren (U. Of Waterloo 1996). The basic theory is that as the clay takes up hydronium ions they break down to produce aluminum, magnesium and iron oxides. The oxides contribute to NP when they react with water to produce hydroxides. The hydroxides in turn react with acid to produce salt and water. The reaction is very slow compared to the NP contribution from calcite.

This test procedure was used by the author in a study where clays were a major part of the mineralogy of potential waste rock. It was found that the clays contributed to the NP in the column cell test work. Clay speciation is very important as to the neutralization potential and must be taken into account for final interpretation and reporting.

Test Procedure

1. Test setup is as per the BCRI Initial Test procedure. The gross weight of the sample, DI water and beaker are measured and recorded.
2. Test is run for 24 h (acid is auto-titrated to pH 3.5) and the acid consumed recorded.
3. Vessel weight is brought back to account for evaporation (account for acid added as well) stood quiescent until a clear supernatant is formed to be sampled for Mg and Mn analysis. 1 mL samples are diluted by a factor of 10. Analyze for magnesium and manganese.
4. Agitation is re-started with the titrator turned off for 8 to 24 hours.
5. pH is recorded and the titrator turned on for 1hour. Volume of acid added is measured and recorded.
6. Step 3 is repeated after adjustment of the vessel weight with DI water to account for evaporation. Take into account the amount removed for Mg analysis (assume 1 mL =1g) and the amount of acid added (determine the density of 1N H2S04).
7. Repeat Steps 4 and 5.
8. Continue with the test repeating steps 6 and 7 until little or no acid is being consumed. This is repeated after 120, 264 and 312 hours.
9. The slurry is filtered and the residue washed with DI water. The solids are air dried and submitted for total sulphur and sulphate sulphur and CO2 analyses. The remaining solids are saved for possible XRD analysis to determine clay species. The leachate water is submitted for each sample for ICP metal analysis.

BC Research Confirmation Test

Objectives

- To confirm the results of static prediction testing
- To determine if sulfide-oxidizing bacteria can generate more acid from a sample than can be consumed

Principles of Test

The acid potential derived by assuming total oxidation of sulfur (sulfides) in static prediction testing may not, under field conditions, be realized. To determine the degree to which the sulfur content of a sample might be oxidized, and to assess if this amount of acid is sufficient to overcome the neutralizing capacity of the sample, a biological oxidation test can be carried out. The test is usually carried out only if the sample is shown to be potentially acid producing in static testing.

A preacidified pulp containing a finely ground test sample is inoculated with an active culture of sulfide-oxidizing bacteria such as *T. ferrooxidans* and agitated under ideal conditions for bacterial oxidation. The pulp pH is monitored until stable, indicating the end of oxidation. A weight equivalent to the original sample is then added in two increments after 24 and 48 h and the pH is measured 24 h after each addition. If the pH is above 3.5 at these times, the sample is classified as a nonacid producer, since the pH is out of the range considered essential for the growth and oxidative activity of the bacteria. If the pH remains below 3.5, a potential for acid generation is indicated.

Equipment

1. 250-mL Erlenmeyer flasks, preferably with a baffled base to facilitate oxygen mass transfer during agitation
2. Temperature-controlled gyratory or reciprocating shaker/incubator equipped with clamps for Erlenmeyer flasks (provision for CO_2 enrichment of the air is desirable)
3. pH meter equipped with a combination pH electrode
4. Pipette, 5 mL

Reagents

1. Sulfuric acid, 6 N or 12 N
2. Distilled or deionized water
3. Reagent-grade nutrient salts, typically $(NH_4)_2SO_4$, KCl, K_2HPO_4, $MgSO_4 \cdot 7H_2O$, and $Ca(NO_3)_2$
4. Bacterial culture containing *T. ferrooxidans* (Cultures should be selected based on their known ability to be able to oxidize ores, waste rock, or tailings of mineralogy similar to that of the test sample.)

Procedure

1. Crush and pulverize the sample to pass a 400-mesh (Tyler) screen.
2. Prepare bacterial cultures for use as inocula using standard laboratory techniques. The cultures should have been grown previously on, and adapted to, ore or waste rock containing pyrite with a sulfur content at least as high as that of the test sample. Whole pulp inocula are preferred to cells recovered from solution only. If solids-free inocula containing very low soluble metal concentrations are

required, these should be prepared by differential centrifugation techniques.

3. In duplicate, weigh out 15 to 30 g (low weight for high sulfur contents) of sample into an Erlenmeyer flask with 70 mL of a nutrient medium containing (typically) 3 g/L $(NH_4)_2SO_4$, 0.1 g/L KCl, 0.5 g/L K_2HPO_4, 0.5 g/L $MgSO_4 \cdot 7H_2O$, and 0.01 g/L $Ca(NO_3)_2$.
4. Place a flask on a shaker and add sulfuric acid (6 or 12 N) periodically as required to bring the pH to a stable value between pH 2.5 and 2.8. Do not proceed until the pH is stable.
5. Inoculate flasks with 5 mL of an active *T. ferrooxidans* culture. Record the weight of the flask, cap the flask with a cotton or foam plug, and place on a shaker at 35°C.
6. Monitor the flask regularly for pH. Before each measurement, add distilled water to bring the flask to its original weight to allow for evaporation. In some cases, the sampling of flasks for a soluble species (e.g., Fe, Cu, Zn) might assist in determining the progress of the oxidation process.
7. When oxidative activity has ceased, as evidenced by a stable pH (or metal concentration), add half the weight of the sample used originally and continue shaking for 24 h.
8. Record the pH, and if above 3.5, terminate the test. If not, again add half the weight of the sample and agitate for up to an additional 72 h and record the final pH.

Typically, about 3 to 4 weeks following inoculation is required to complete this test.

Interpretation of Results

A decreasing pH following inoculation of the test pulp with bacteria indicates the biochemical oxidation of sulfides contained in the sample. Once a stable pH or soluble metal concentration has been achieved, it is assumed that all sulfide available for oxidation has reacted and that the maximum acidity has been generated. By adding more sample equal to the original weight after reaction and observing the pH change, the ability of the sample to generate acid in excess of its neutralizing capacity can be assessed. Specifically, the sample is confirmed to be an acid producer if the pH remains below 3.5. Above this pH, biochemical oxidation is considered to be unlikely, and the sample is classified as a nonacid producer.

Reporting of Results

The results of the test should be tabulated to provide the following information: sample description, test duration (days after inoculation), initial pH, pH after biological oxidation, pH after first increment of sample addition, pH after second increment of sample addition (final pH), and confirmation of acid production potential (yes/no).

Advantages of Test

- Relatively low cost and rapid kinetic test
- Has been used widely in Canada
- Provides an assessment for the potential of biochemical oxidation

Disadvantages of Test

- Although the procedure is apparently simple, tests involving the use of bacteria require experience and can have problems of (1) nonoptimum use of cultures, (2) use of nonadapted cultures, and (3) difficulties of comparing results between laboratories.

- The acidification procedure creates an unrealistic condition in that the inhibitory effects of the alkaline components of the waste on oxidation reactions are not evaluated, and the method does not allow evaluation or modeling of the initial ARD production stages in the upper pH ranges.
- The amount of acid generated in the test is not corrected for the initial acid added to bring the pH into a range suitable for inoculation. This can bias the result toward an acid classification.
- For samples with high sulfur contents, the amount of sample required by the test procedure might be too large, leading to incomplete oxidation of the sulfur available, due to inhibition of reaction by reaction products and low pH.

Original Reference

Bruynesteyn, A., and Hackl, R.P., 1984. Evaluation of acid production potential of mining waste materials. Minerals and the Environment, vol. 4, no. 1, pp. 5–8.

Coastech Modified Biological Oxidation Test

Some of the disadvantages of the BC Research Confirmation Test can be reduced by adopting the following modifications of the standard procedure. The modified test has been used routinely for a number of years. Table 20.1 summarizes the sample weights for various sample sulfur contents. The initial sample weight is selected on the basis of the sulfur content (basis: 50 mL nutrient solution).

Table 20.1 Sample Weight for Various Sample Sulfur Contents, Coastech Modified Biological Oxidation Test

% Sulfur	Sample Weight (g)
<4	10.0
4–8	7.5
8–15	5.0
>15	3.0

Source: Lawrence and Sadeghnobari (1986).

At the end of the test, following the full addition of extra sample, if the pH is still below 3.5, sodium hydroxide solution (3 to 6 N) is added to the pulp, stoichiometrically equivalent to the acid added initially to bring the pH into the biochemical oxidation range. The final pH is recorded after 1 h. This procedure removes the bias toward an acid classification.

Original Reference

Lawrence, R.W., and Sadeghnobari, A., 1986. In-House Development of a Modified Biological Confirmation Test for AMD Prediction. Coastech Research, West Vancouver, BC, Canada. See also: Lawrence, R.W., Poling, G.W., and Marchant, P.B., 1989. *Investigation of Predictive Techniques for Acid Mine Drainage*. Final Report on DSS Contract 23440-7-9178/01-SQ, MEND Report 1.16.1(a). Energy, Mines, and Resources, MEND, Ottawa, ON, Canada.

Lapakko Procedure For The Determination Of Neutralizing Potential Of Metal Mine Waste

The method used is a modification of the BC Research Initial Test. The major difference between the two methods is the use of a pH 6.0 endpoint instead of pH 3.5.

Sample Preparation

Grind or pulverize the sample to 70% passing a 325 mesh (i.e., 70% of particles should have a diameter of less than 44 μm).

Titration Test

Prepare a stirred mixture of 10 g of sample in 100 mL of distilled water. Using an automatic titrator (Type 45 AR Chemtrix pH controllers with Cole Parmer electrodes were used for the original work), titrate with 1.0 N sulfuric acid until a pH of 6.0 is reached. The test is complete when less than 0.1 mL of acid is added over a 4-h period.

Notes (Kim Lapakko)

The alternative method of NP determination proposed is the same as the BC Research initial test, except that a titration endpoint of 6.0 was used in the present study rather than 3.5. pH 6 was selected since it is a commonly applied water quality standard. Therefore, the neutralization potential available above this pH represents the amount of acid that a mine waste could neutralize while maintaining a drainage pH in a range that meets water quality standards.

It should be noted that this method is intended for the NP present rather than the NP available for reaction in the field. Consequently, the value determined for waste rock will exceed that which is practically available in the field. This is the natural consequence of not running the test on field-size particles, which would consider the mode of occurrence of neutralizing minerals. It is just a bit difficult to squeeze some of that field-size material into these beakers. Nonetheless, for future testing I would consider using a larger particle size for waste rock. In our lab we have made the additional modification of using 2 g rather than 10 g in the test. For some solids, the procedure can be quite slow (Lawrence and Wang, 1996). This is particularly the case for elevated carbonate contents and cases where the carbonate occurs with magnesium or magnesium and iron mixtures.

Original Reference

Lapakko, K., 1994. Evaluation of neutralization potential determinations for metal mine waste and a proposed alternative. In: Proceedings of the International Land Reclamation and Mine Drainage Conference, Pittsburgh, PA. special pubnlication SP 06A-94. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 129–137.

Neutralization Potential: EPA (Sobek) Method

Principles

The amount of neutralizing bases, including carbonates, present in overburden materials is found by treating a sample with a known excess of standardized hydrochloric acid. The sample and acid are heated

to ensure that the reaction between the acid and the neutralizers goes to completion. The calcium carbonate equivalent of the sample is obtained by determining the amount of unconsumed acid by titration with standardized sodium hydroxide.

Comments

A fizz rating of the neutralization potential is made for each sample to ensure the addition of sufficient acid to react all the calcium carbonate present. During digestion, do not boil samples. If boiling occurs, discard the sample and rerun. Before titrating with acid, fill a burette with acid and drain completely. Before titrating with base, fill the burette with base and drain completely to assure that free titrant is being added to the sample.

Chemicals

1. Carbon dioxide–free water: Heat distilled water in a beaker just to boiling. Allow the water to cool slightly and pour into a container equipped with an ascarite tube. Cool to room temperature before using.
2. Hydrochloric acid (HCl) solution, 0.1 N, certified grade (Fisher So-A-54 or equivalent).
3. Sodium hydroxide (NaOH), approximately 0.5 N: Dissolve 20.0 g of NaOH pellets in carbon dioxide–free water and dilute to 1 L. Protect from CO_2 in the air with an ascarite tube. Standardize the solution by placing 50 mL of certified 0.1 N HCl in a beaker and titrating with the prepared 0.5 N NaOH until a pH of 7.00 is obtained. Calculate the normality of the NaOH using the equation

$$N_2 = \frac{N_1 V_1}{V_2}$$

   where V_1 is the volume of HCl used, N_1 the normality of HCl used, V_2 the volume of NaOH used, and N_2 the calculated normality of NaOH.
4. Sodium hydroxide (NaOH) approximately 0.1 N: Dilute 200 mL of 0.5 N NaOH with carbon dioxide–free water to a volume of 1 L. Protect from CO_2 in the air with an ascarite tube. Standardize the solution by placing 20 mL of certified 0.1 N HCl in a beaker and titrating with the prepared 0.1 N NaOH until a pH of 7.00 is obtained. Calculate the normality of the NaOH.
5. Hydrochloric acid (HCl), approximately 0.5 N: Dilute 42 mL of concentrated HCl to a volume of 1 L with distilled water. Standardize the solution by placing 20 mL of the known-normality NaOH prepared in a beaker and titrating with prepared HCl until a pH of 7.00 is obtained. Calculate the normality of the HCl using the equation

$$N_1 = \frac{N_2 V_2}{V_1}$$

   where V_2 is the volume of HCl used, N_2 the normality of NaOH used, V_1 the volume of HCl used, and N_1 the calculated normality of HCl.
6. Hydrochloric acid (HCl), approximately 0.1 N: Dilute 200 mL of 0.5 N HCl to a volume of 1 L with distilled water. Standardize the solution as before, but use 20 mL of the known-normality NaOH.
7. Hydrochloric acid (HCl), 1 part acid to 3 parts water: Dilute 250 mL of concentrated HCl with 750

mL of distilled water.

Materials

1. Flasks, Erlenmeyer, 250 mL.
2. Burette, 100 mL (one required for each acid and one for each base).
3. Hot plate; steam bath may be substituted.
4. pH meter (Corning Model 12 or equivalent) equipped with a combination electrode.
5. Balance; can be read to 0.01 g.

Procedure

1. Place approximately 0.5 g of the sample (less than 60 mesh) on a piece of aluminum foil.
2. Add 1 or 2 drops of 1 : 3 HCl to the sample. The presence of $CaCO_3$ is indicated by a bubbling or audible “fizz.”
3. Rate the bubbling in step 2 as indicated in Table 20.2.
4. Weigh 2.00 g of sample (less than 60 mesh) into a 250-mL Erlenmeyer flask.
5. Carefully add HCl as indicated by Table 20.2 into the flask containing the sample.
6. Heat nearly to boiling, swirling the flask every 5 min, until the reaction is complete. Note: The reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask.
7. Add distilled water to make a total volume of 125 mL.
8. Boil the contents of the flask for 1 min and cool to slightly above room temperature. Cover tightly and cool to room temperature. *Caution*: Do not place a rubber stopper in a hot flask, as it may implode upon cooling.
9. Titrate using 0.1 or 0.5 N NaOH (concentration known exactly) to pH 7.00 using an electrometric pH meter and burette. The concentration of NaOH used in the titration should correspond to the concentration of the HCl used in step 5. *Note:* Titrate with NaOH until a constant reading of pH 7.0 remains for at least 30 seconds.
10. If less than 3 mL of the NaOH is required to obtain a pH of 7.0, it is likely that the HCl added was not sufficient to neutralize all of the base present in the 2.00 g of sample. A duplicate sample should be run using the next-higher volume or concentration of acid, as indicated in Table 20.2.
11. Run a blank for each volume or normality using steps 5, 7, 8, and 9.

Table 20.2 Volume and Normality of Hydrochloric Acid Used for Each Fizz Rating

Fizz Rating	HCl (mL)	HCl (Normality)
None	20	0.1
Slight	40	0.1
Moderate	40	0.5
Strong	80	0.5

Source: Sobek et al. (1978).

Calculations

1. Constant (C) = (mL acid in blank)/(mL base in blank).
2. mL acid consumed = (mL acid added) − (mL base added × C).
3. Tons $CaCO_3$ equivalent/thousand tons of material = (mL of acid consumed) × 25.0 × (N of addition).

Original Reference

Sobek, A., Schuller, W.A., Freeman, J.R., and Smith, R., 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoil. EPA-600/2-78-054. West Virginia University, College of Agriculture and Forestry, Morgantown, WV, pp. 47–50.

Static Net Acid Generation Procedure

Sample Preparation

Drill core and bulk rock samples should be crushed to a nominal 4 mm and a subsample pulverized to approximately 200 mesh (<75 µm). Tailing and process residue samples can be tested ``as received."

Reagents

1. H_2O_2—BDH Analar analytical reagent 30% w/v (100 v), or equivalent, diluted 1 : 1 with deionized H_2O to 15%. (Refer to Note 1.)
2. NaOH—0.50 M standardized solution.
3. NaOH—0.10 M standardized solution.

Method

1. Add 250 mL of reagent 1 (15% H_2O_2) to 2.5 g of pulverized sample in a 500-mL wide-mouth conical flask, or equivalent. Cover with a watch glass and place in a fumehood or well-ventilated area (refer to Note 2). The H_2O_2 should be at room temperature before beginning the test.
2. Allow the sample to react until “boiling” or effervescing ceases. Heat the sample on a hot plate and gently boil until effervescence stops, or for a minimum of 2 h. Do not allow the sample to boil dry—add deionized water if necessary.
3. Allow solution to cool to room temperature, then record final pH (net acid generation pH).

4. Rinse the sample that has adhered to the sides of the flask down into the solution using deionized water. Add deionized water to give a final volume of 250 mL. Table 20.3 shows the NaOH concentration required for titration in a static net acid generation (NAG) procedure.
5. Titrate the solution to pH 4.5 while stirring with the appropriate NaOH concentration based on the final NAG solution pH.

Table 20.3 NaOH Concentration Required for Titration, Static Net Acid Generation Procedure

NAG Solution pH	Reagent	NaOH Concentration
>2	3	0.10 M
<2	2	0.50 M

Source: Miller et al. (1997).

Calculation of Net Acid Generation

$$\mathrm{NAG} = 49 \times V \times M / W$$

where NAG is the net acid generation [kg H_2SO_4/metric ton (mt)], V the volume of base NaOH titrated (mL), M the molarity of base NaOH (mol/L), and W the weight of sample reacted (g). *Note:* If the NAG value exceeds 25 kg H_2SO_4/mt, repeat using a 1.00-g sample.

Notes and Precautions

1. The pH of the H_2O_2 used in the NAG test should be checked to ensure that it is between pH 4 and 7. If the pH is less than 4, add dilute NaOH (use a solution made up by adding 1 g of NaOH to 100 mL of deionized H_2O) until the pH is greater than 4 (aim for a pH between 4 and 6). The pH is adjusted to greater than pH 4 to ensure that the phosphoric acid used to stabilize H_2O_2 in some brands is neutralized. The pH of the 15% H_2O_2 should always be checked to ensure that any stabilizing acid is neutralized; otherwise, false-positive results may be obtained.
2. The NAG reaction can be vigorous, and sample solutions can “boil” at temperatures of up to 120°C. Great care must be taken to place samples in a well-ventilated area or fume cupboard.
3. Caution should be taken in the interpretation of NAG test results for coal reject samples and other materials that may have a high organic material content (such as potential acid sulfate soils, dredge sediments, and other lake or marine sediments). All organic material must be oxidized completely; otherwise, acid NAG results can occur which are unrelated to sulfides. Several aliquots of H_2O_2 reagent may be added to the sample to break down any organic acidity.
4. Samples with positive NAPP value, high sulfur content, and high ANC must be evaluated carefully.

References

Miller, S., Robertson, A., and Donahue, T., 1997. Advances in acid drainage prediction using the net acid generation (NAG) test. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, 0533-549. See also: Lawrence, R.W., Jaffe, S., and Broughton, L.M., 1988. In-House Development of the Net Acid Production Test Method. Coastech Research, West Vancouver, BC, Canada.

Modified Acid–Base Accounting Procedure For Neutralization Potential (Lawrence)

1. Add a few drops of 25% HCl to 1 to 2 g of pulverized sample on a watch glass or piece of aluminum foil. Observe the degree of reaction and assign a fizz rating: none, slight, moderate, or strong.
2. Weigh approximately 2.00 g of pulverized sample into a 250-mL conical flask and add approximately 90 mL of distilled water. Table 20.4 shows the fizz rating for a modified acid–base accounting procedure for neutralization potential.
3. At the beginning of the test (time = 0), add a volume of certified or standardized 1.0 N HCl according to the fizz rating.
4. Place the flask on a shaking apparatus such as a reciprocating shaker, maintained at room temperature. After approximately 2 h, add the second acid quantity as indicated in Table 20.4.
5. After approximately 22 h, check the pH of the pulp. If it is greater than 2.5, add a measured volume of 1.0 N HCl to bring the pH into the range 2.0 to 2.5. If the pH is less than 2.0, too much acid was added in steps 2 and 3. In this case, repeat the test, adding a reduced volume of HCl.
6. After 24 h, terminate the test and add distilled water to the flask to bring the volume to approximately 125 mL. Measure and record the pH, making sure that it is in the required range of 2.0 to 2.5.
7. Titrate the contents of the flask to a pH of 8.3 using certified or standardized 0.5 or 0.1 N NaOH.
8. Calculate the NP of the sample as follows:

$$\text{modified NP (kg } CaCO_3/\text{mt)} = \frac{[\text{N} \times \text{vol(mL) of HCl}] - [\text{N} \times \text{vol (mL) NaOH}) \times 50]}{\text{weight of sample (g)}}$$

Table 20.4 Volume of HCl Added for Various Fizz Ratings: the Modified Acid–Base Accounting Procedure for Neutralization Potential (Lawrence)

	Volume of 1.0 N HCl (mL)	
Fizz Rating	**At Time = 0 h**	**At Time = 2 h**
None	1.0	1.0
Slight	2.0	1.0
Moderate	2.0	2.0
Strong	3.0	2.0

Source: Lawrence and Wang (1997).

The acid-generating potential of the sample should be calculated on the basis of the sulfide-sulfur content ($AP = S^{2-} \times 31.25$). Sulfide-sulfur is typically determined as the difference between total sulfur and sulfate sulfur, although analysis of other sulfur species, such as elemental sulfur and barite sulfur, is sometimes justified. Caution should be exercised for certain samples in interpreting sulfate-sulfur analyses, as this form can be either inert (e.g., gypsum) or essentially stored products of acid drainage that could become mobilized if conditions within a waste change. Reference to MEND Report 1.16.1c is suggested (Norecol Environmental Consultants, 1991) for a discussion of sulfur species.

Reference

Lawrence, R.W., and Wang, Y., 1997. Determination of neutralization potential in the prediction of acid rock drainage. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 449–464. See also: Coastech Research, 1991. Acid Rock Drainage Prediction Manual. MEND Project Report 1.16.1b. MEND, Ottawa, ON, Canada.

Peroxide Siderite Correction For Sobek Method

The following discussion and method are taken from Skousen et al. (1997) and adapted with the kind permission of the authors.

Discussion

Meek (1981) suggested that the NP of certain rock units is overestimated when siderite ($FeCO_3$) is present. Siderite, along with calcite and dolomite, is a common carbonate mineral in the overburden associated with Appalachian coal beds (Cecil et al., 1985; Morrison et al., 1990b). Even though natural weathering of siderite is a slow process, siderite will react if exposed to the aqueous and acidic conditions used in the laboratory to determine NP (Doolittle et al., 1992). When present in an overburden sample, siderite reaction with acid contributes to the apparent alkaline-producing potential of the rock (Meek, 1981; Morrison et al., 1990a; Wiram, 1992). Continued weathering of siderite, however, produces a neutral (Meek, 1981; Shelton et al., 1984) to slightly acid solution, as indicated in the following reaction (Postma, 1983; Cravotta, 1991; Doolittle et al., 1992; Frisbee and Hossner, 1995).

$$FeCO_3 + \tfrac{1}{4}\,O_2 + 2\tfrac{1}{2}\,H_2O = Fe(OH)_3 + H_2CO_3 \tag{20.1}$$

where $H_2CO_3 = H_2O + CO_{2(aq)}$.

In the laboratory determination of NP in ABA, many reaction steps during the titration can affect the pH. The first step in the reaction of siderite with excess hydrochloric acid (HCl) is

$$FeCO_3 + 2HCl = Fe^{2+} + 2Cl^- + H_2O + CO_2 \tag{20.2}$$

Because the solution is acidic, the CO_2 is exsolved as a gas. The ferrous iron (Fe^{2+}) produced by reaction (20.2) is also unstable and will slowly oxidize to ferric iron (Fe^{3+}) and consume additional HCl:

$$Fe^{2+} + \tfrac{1}{4}O_2 + HCl = Fe^{3+} + Cl^- + \tfrac{1}{2}H_2O \tag{20.3}$$

The ferric iron (Fe^{3+}) produced will consume base ions upon titration with sodium hydroxide (NaOH) and precipitate as ferric hydroxide:

$$Fe^{3+} + 3NaOH = Fe(OH)_3 + 3Na^+ \tag{20.4}$$

The overall reaction is essentially reaction (20.1) with the addition of sodium (Na^+) and chloride (Cl^-):

$$FeCO_3 + \tfrac{1}{4}O_2 + 3HCl + 3NaOH = Fe(OH)_3 + 3Na^+ + 3Cl^- + 1\tfrac{1}{2}H_2O + CO_2(g) \tag{20.5}$$

Reaction (20.5), which represents the major reactants and products for NP digestion and titration, shows that 3 mol of acidity (HCl) and 3 mol of base (NaOH) are consumed and that CO_2 is exsolved. As a result, the overall reaction yields a zero NP for siderite (no net acidity or alkalinity). Because the standard NP procedure as outlined by Sobek et al. (1978) does not allow sufficient time for ferrous iron oxidation and subsequent precipitation of ferric hydroxide, the procedure accounts for only the initial reaction, resulting in 3 mol of alkalinity [reactions (20.2) and (20.3)]. Therefore, erroneously high NP values can be generated with samples containing high amounts of siderite. Such an analytical oversight can lead to incorrect postmining water quality predictions, result in premature mine closure, and produce costly, long-term reclamation liabilities for mining companies (Wiram, 1992).

Meek (1981) was the first to suggest adding a small quantity of 30% hydrogen peroxide (H_2O_2) to the filtrate of an HCl-digested siderite overburden sample to oxidize ferrous iron to ferric iron before backtitration. Because the resulting ferric iron is precipitated as $Fe(OH)_3$ upon titration, the solution yields a more accurate NP value. The addition of H_2O_2 after the initial titration results in the formation of additional $Fe(OH)_3$, due to enhanced oxidation at higher pH values.

Method

The method, developed by a Pennsylvania–West Virginia Overburden Task Force (Leavitt et al., 1995), is as follows (for triplicate samples and a blank):

1. Place a 2-g sample in each of three beakers, with a fourth beaker having no sample.
2. Add an amount and strength of HCl to each beaker based on the sample fizz rating, and adjust the volume to 100 mL.
3. Add boiling chips to the beakers and cover with a watch glass.
4. Boil gently for 5 min, then allow to cool.
5. Gravity-filter the beaker contents using a Whatman No. 40 (0.45-µm) filter.
6. Add 5 mL of 30% H_2O_2 to the filtrate.
7. Boil a further 5 min (boiling chips and watch glasses), then cool.
8. Hand-titrate, according to the Sobek method, with standard NaOH to achieve and hold an endpoint pH of 7.0 for 30 s.

Original Reference

Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L., and Ziemkiewicz, P., 1997. Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, vol. 26, no. 3, pp. 673–681.

Paste pH

The procedure for paste pH given here is that currently recommended by the British Columbia Ministry of Employment and Investment, Energy and Minerals Division (Price, 1997). It is based on the method of Sobek et al. (1978), with modifications by Page et al. (1982) and others. Modifications of Sobeks method are shown in italic.

Care must be taken to ensure electrode life and accurate pH measurements:

1. The electrode should not remain in the sample longer than necessary for a reading, especially if more alkaline than pH 9.0 *or more acidic than pH 2.0.*
2. The electrode should be washed with a jet of distilled water from a wash bottle after every measurement (sample or buffer solution).
3. The electrode should be dipped in dilute (*0.1 N*) hydrochloric acid for a few seconds and washed with distilled water to remove any calcium carbonate film that may form, especially from alkaline samples.
4. Drying out of the electrode should be avoided.
5. The electrode is cleaned and suspended in distilled water (which is protected from evaporation) for storage.
6. Place the pH meter in standby position when the electrode is not in a solution.

The pH meter and electrode should be standardized with buffers differing by 3 or 4 pH units, such as 7.0 and 4.0, before beginning a series of measurements. After every tenth measurement, recheck the standardization with both buffers. Care should be taken not to contaminate one buffer with the other buffer or with the test solution. Never return used standard buffers to their stock bottles.

Chemicals

1. Standard buffer solutions, pH 4.00 and 7.00
2. Distilled water (H_2O)

Materials

1. pH meter equipped with a combination electrode.
2. Paper cups, 30 mL capacity.
3. Plastic cups.
4. Stirring rod.
5. Wash bottle containing distilled water.
6. Balance, can be read to 0.1 g.

Procedure

(1 : 1 Solid/Solution Ratio)

1. Turn on the pH meter, adjust the temperature setting, and “zero” the pH meter following the instruction manual.
2. Place pH 4.0 and 7.0 standard buffers in two plastic cups (one buffer in each cup).

   (*Note:* Never return used buffers to stock bottles.)
3. Place the electrode in the pH 7.0 buffer.
4. Adjust the pH meter to read 7.0.
5. Remove the electrode from the buffer solution and wash with a jet of distilled water from a wash

bottle.

6. Place the electrode in the pH 4.0 buffer and check the pH reading.

   Note: If the pH meter varies by more than ±0.1 pH unit from 4.0, something is wrong with the pH meter, electrode, or buffers.

   Note: The following is adapted from Page et al. (1982).

7. Weight or measure *20 g* of air-dry *test material and 20 mL of distilled water.*
8. Mix thoroughly for 5 s, preferably with a portable mechanical stirrer.
9. Let stand for l0 min.
10. Insert the electrode(s) into the container, and stir the *supernatant* by swirling the electrodes slightly. *Protect the electrodes, taking care not to contact sealed particles, moving the electrode carefully about to ensure removal of water film around the electrode. Electrodes are easily scratched.*
11. *When reading remains constant, record the pH and remove the electrode from the supernatant. Carefully wash the electrode with distilled water. If all the pH measurements are completed, the electrode should be stored in a beaker of distilled water. (Note: After every 10 samples, check the meter calibration with standard buffers.)*

References

Alforque, M., 1996. Synthetic Precipitation Leaching Procedure. U.S. Environmental Protection Agency, Washington, DC.

Bruynesteyn, A., Duncan, D.W., 1979. Determination of acid production potential of waste materials. Presented at the AIME Annual Meeting, New Orleans, LA, February, 19–21, paper A-79-29. Minerals and the Environment, 1982, vol. 4, no. 1, pp. 5–8.

Cecil, C.B., Stanton, R.W., Neuzil, S.G., Dulong, F.T., Ruppert, L.F., and Pierce, B.S., 1985. Paleoclimatic controls on late Paleozoic sedimentation and peat formation in the Central Appalachian Basin (U.S.A.). International Journal of Coal Geology, vol. 5, pp. 195–230.

Coastech Research, 1989. Investigation of Prediction Techniques for Acid Mine Drainage. MEND Project Report 1.16.1a. West Vancouver, BC, Canada.

Coastech Research, 1991. Acid Rock Drainage Prediction Manual. MEND Project Report 1.16.1b. West Vancouver, BC, Canada.

Cravotta, C.A., III, 1991. Geochemical evaluation of acidic ground water at a reclaimed surface coal mine in western Pennsylvania. In: Proceedings of the 1991 National Meeting of the American Society for Surface Mining and Reclamation, Durango, CO, May 14–17. American Society for Surface Mining and Reclamation, Princeton, WV, pp. 43–68.

Day, S.J., 1991. New Methods for Determination of Key Mineral Species in Acid Generation Prediction by Acid–Base Accounting, MEND Project Report 1.16.1c. MEND, Ottawa, ON, Canada.

Doolittle, J.J., Frisbee, N.M., and Hossner, L.R., 1992. Evaluation of acid-base accounting techniques used in surface-mine reclamation. In: Proceedings of the 1992 Meeting of the American Society of Surface Mining and Reclamation, June 14–18, Duluth, MN, pp. 68–76.

Downing, B.W., and Madeisky, H.E., 1997. Acid rock drainage study of the ovoid zone: Voisey's Bay Project. Presented at the 4th International Conference on Acid Mine Drainage, Vancouver, BC, Canada, 10 pp.

Duncan, D.W., and Bruynesteyn, A., 1979. Determination of Acid Production Potential of Waste Materials. Paper A79-29. Metallurgical Society AIME, New York, l0 pp.

Erickson, P.M., and Hedin, R., 1988. Evaluation of Overburden Analytical Methods as a Means to Predict Postmining Coal Mine Drainage Quality. Information Circular 9183. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 11–19.

Finkelman, R.B., and Giffin, D.E., 1986. Hydrogen peroxide oxidation: an improved method for rapidly assessing acid-generating potential of sediments and sedimentary rocks. Recreation and Revegetation Research, vol. 5, pp. 521–34.

Frisbee, N.M., and Hossner, L.R., 1995. Siderite weathering in acidic solutions under carbon dioxide, air and oxygen. Journal of Environmental Quality, vol. 24, pp. 856–860.

Lawrence, R.W., 1995. Prediction of acid rock drainage: fundamentals and tools. Presented at the MEND Prediction Workshop, Montreal, December 7–8. MEND, Ottawa, ON, Canada, 27 pp.

Lawrence, R.W., and Sadeghnobari, A., 1986a. In-House Development of a Modified Acid–Base Accounting Procedure. Coastech Research, West Vancouver, BC, Canada.

Lawrence, R.W., and Sadeghnobari, A., 1986b. In-House Development of a Modified Biological Confirmation Test for AMD Prediction, Coastech Research, West Vancouver, BC, Canada.

Lawrence, R.W., and Wang, Y., 1996. Determination of Neutralization Potential for Acid Rock Drainage Prediction. MEND Project Report 1.16.3. MEND, Ottawa, ON, Canada.

Lawrence, R.W., and Wang, Y., 1997. Determination of neutralization potential in the prediction of acid rock drainage. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 449–464.

Lawrence, R.W., Jaffe, S., and Broughton, L.M., 1988. In-House Development of the Net Acid Production Test Method. Coastech Research, West Vancouver, BC, Canada.

Lawrence, R.W., Poling, G.W., and Marchant, P.B., 1989a. Investigation of Prediction Techniques for Acid Mine Drainage. DSS Contract 23440-7-9178/01-SQ, Final Report. MEND, Ottawa, ON, Canada.

Lawrence, R.W., Ritcey, G.M., Poling, G.W., and Marchant, P.B., 1989b. Strategies for the prediction of acid mine drainage. In: Proceedings of the 13th Annual Mine Reclamation Meeting, Vernon, BC, Canada, June 7–9.

Leavitt, B.J., Skousen, J., and Ziemkiewicz, P., 1995. Effects of siderite on the neutralization potential in the acid–base account. In: Proceedings of the 17th Annual West Virginia Surface Mine Drainage Task Force Symposium, April 4–5, West Virginia University, Morgantown, WV.

Meek, F.A., 1981. Development of a procedure to accurately account for the presence of siderite during mining overburden analysis. In: Proceedings of the 2nd Annual West Virginia Surface Mine Drainage Task Force Symposium, April 27, West Virginia University, Morgantown, WV.

Miller, S., Robertson, A., and Donahue, T., 1997. Advances in acid drainage prediction using the net acid generation (NAG) test. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 533–549.

Morrison, J.L., Atkinson, S.D., Davis, A., and Scheetz, B.E., 1990a. The use of CO_2 coulimetry in differentiating and quantifying the carbonate phases in coal-bearing strata of western Pennsylvania: its applicability in interpreting and modifying neutralization potential (NP). In: Proceedings of the 1990 Meeting of the American Society for Surface Mining and Reclamation, J. Skousen et al., eds., April 23–26, West Virginia University, Morgantown, WV, pp. 243–247.

Morrison, J.L., Scheetz, B.E., Strickler, D.W., Williams, E.G., Rose, A.W., Davis, A., and Parizek, R.R., 1990b. Predicting the occurrence of acid mine drainage in the Alleghenian coal-bearing strata of western Pennsylvania: an assessment by simulated weathering (leaching) experiments and overburden characterization. In: Recent Advances in Coal Geochemistry, L.L. Chyi, and C. Chou, eds. Special Paper 248. Geological Society of America, Denver, CO.

Norecol Environmental Consultants, Ltd., 1991. New Methods for Determination of Key Mineral Species in Acid Generation Prediction by Acid–Base Accounting. Mine Environment Neutral Drainage Report 1.16.1c. MEND, Vancouver, BC, Canada, 100 pp.

Page, A.L., Miller, R.H., and Keeney, D.R., 1982. Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, 2nd edn. American Society of Agronomy and Soil Science Society of America, Madison, WI, pp. 199–209.

Postma, D., 1983. Pyrite and siderite oxidation in swamp sediments. Journal of Soil Science, vol. 34, pp. 163–192.

Price, W.A., 1997. Draft: Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia. British Columbia Ministry of Employment and Investment, Energy and Minerals Division, Smithers, BC, Canada, 143 pp.

Price, W.A., and Errington, J.C., 1995. ARD Guidelines for Mine Sites in British Columbia. British Columbia Ministry of Energy, Mines and Petroleum Resources, Victoria, BC, Canada, 29 pp.

Price, W.A., and Kwong, Y.T.J., 1997. Waste rock weathering, sampling and analysis: observations from the British Columbia Ministry of Employment and Investment database. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 31–45.

Price, W.A., Morin, K., and Hutt, N., 1997. Guidelines for the prediction of acid rock drainage and metal leaching for mines in British Columbia; Part II, Recommended procedures for static and kinetic testing. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 15–30.

Province of British Columbia, 1992. Waste Management Act: Special Waste Regulation Schedule 4, Parts 1 and 2. Queen's Printer, Victoria, BC, Canada, pp. 72–79.

Shelton, P.A., Ammons, J.T., and Freeman, J.R., 1984. Neutralization potential: a closer look. Green Lands, vol. 13, no. 4, pp. 35–37.

Sherlock, E.J., Lawrence, R.W., and Poulin, R., 1995. On the neutralization of acid rock drainage by carbonate and silicate minerals. Environmental Geology, vol. 25, pp. 43–54.

Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L., and Ziemkiewicz, P., 1997. Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, vol. 26, no. 3, pp. 673–681.

Sobek, A.A., Schuller, W.A., Freeman, J.R., and Smith, R.M., 1978. Field and Laboratory Methods Applicable to Overburden and Minesoils. Report EPA-600/2-78-054, U.S. National Technical Information Service Report PB-280 495. U.S. EPA, Washington, DC.

Soregaroli, B.A., and Lawrence, R.W., 1997. Waste rock characterization at Dublin Gulch: a case study. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 631–645.

Steffen, Robertson and Kirsten (BC), Inc. and BC Research and Development, 1992. Guidelines for Acid Rock Drainage Prediction in the North. Indian and Northern Affairs Canada, Ottawa, ON, Canada.

Wiram, V.P., 1992. ``Siderite masking'': a factor to consider in overburden acid–base balancing. In: Proceedings of the 13th Annual West Virginia Surface Mine Drainage Task Force Symposium, April 8–9, West Virginia University, Morgantown, WV.

The following procedures are in use, or have been used, as part of ARD prediction programs to determine the nature and quantities of soluble constituents that may be washed from materials under natural precipitation conditions: rainwater and snowmelt (meteoric water). I would like to thank my colleague Brian Soregaroli, formerly of Klohn Crippen, for assistance in the preparation of this material.

Meteoric Water Mobility Procedure: Standardized Column Percolation Test Procedure

This is an amended version of the meteoric water mobility procedure proposed by the Nevada Mining Association in January 1996.

Scope

The purpose of the meteoric water mobility procedure (MWMP) is to evaluate the potential for dissolution and mobility of certain constituents from a mine rock sample by meteoric water. The procedure consists of a single-pass column leach over a 24-h period using a mine rock sample/extraction fluid (effluent) ratio of 1 : 1. The extraction fluid is type II reagent-grade water.

Reference Documents

1. Meteoric Water Mobility Procedure, Bureau of Mining Regulation and Reclamation, Nevada Division of Environmental Protection, September 19, 1990.

2. Standard Methods for the Examination of Water and Wastewater, 18th ed., APHA/AWWA/WEF, 1992, Method 1080.

Significance and Use

1. This procedure is intended as a means of obtaining extracts from mine rock samples. The extracts may be used to evaluate the final pH and release of certain constituents of mine rock exposed to meteoric

events.

2. The pH of the extraction fluid used in this procedure is to reflect the pH of precipitation in the geographic region in which the mine rock is being evaluated (in this case, the state of Nevada).
3. This procedure is designed to mobilize potential contaminants present in the solids, so that the resulting extract can be used to assess leachate which could potentially be produced from mine rock in the field.
4. This procedure produces extracts that are amenable to the determination of both major and minor (trace) constituents. When minor constituents are being determined, it is especially important that precautions be taken in sample storage and handling to avoid possible contamination of the samples.
5. This procedure may not be suitable for obtaining extracts from finely divided solids (e.g., clayey soils, sludges, mill tailings). An alternative extraction procedure may then be advised.

Apparatus

1. *Extraction device*: PVC column of 15 cm (6 in.) OD of sufficient height to contain a minimum of 5 kg of −5-cm (2-in.) mine rock sample and sufficient additional height to contain applied extraction fluid should blinding (ponding) occur. (Approximately 8 kg of −5-cm solids per 30.5 cm of column height). For a 5-kg mine rock sample, a 15-cm-OD × 45-cm-high column is recommended. Additional column height will be required for mine rock sample quantities greater than 5 kg. The bottom of the column must be sealed (bubble cap) and a solution discharge outlet situated above the sealed bottom of the column and below the punch plate.
2. *Glass wool* (inert): placed onto the punch plate before loading the mine rock charge into the column to minimize fines migration and onto the top of the mine rock charge after column loading to aid even extraction fluid distribution.
3. *Metering pump* or *constant-head device*: to ensure constant-rate-extraction fluid application.
4. *Extraction fluid* (influent) and *effluent containers:* sufficient in size to contain liquid used during extraction. Containers must be covered to avoid possible contamination from sources outside the test apparatus.
5. *Laboratory balance*: capable of weighing to 1.0 g.
6. *Drying pans* or *dishes*: for moisture-content determinations.
7. *pH meter*: with a readability of 0.01 unit and an accuracy of ±0.05 unit at 25°C.
8. *Filtration assembly device*: of a composition suitable to the nature of the analyses to be performed and equipped with a filter of 0.45-µm pore size. An assembly for prefiltration or centrifugation may be required if 0.45-µm filtration is difficult.
9. *Surgical or Tygon tubing*: sufficient in diameter and length for the extraction device assembly (pump, column effluent outlet).

Reagents

Water purified by distillation, ion exchange, reverse osmosis, electrodialysis, or a combination thereof, conforming to the specifications for type II reagent-grade water.

Sampling (Field)

1. Field sampling should be accomplished to ensure that a representative mine rock sample is obtained.
2. The minimum quantity of mine rock sample required for the MWMP is 5 kg. At least 7 kg of mine rock sample should be submitted to the laboratory for feed moisture content determination, MWMP, and other potential analyses requested by the submitting company. Mine rock samples of up to 25 kg are appropriate for submittal.
3. It is important that the mine rock sample be representative with respect to surface area, as variations in surface area may directly affect the leaching characteristics of the sample. Mine rock samples should contain a representative distribution of particle sizes.
4. Keep samples in closed containers (bags, buckets) appropriate to sample type and analysis for transport to the laboratory.

Sample Preparation (Laboratory)

1. Remove the mine rock sample from the container and blend by coning or rolling and obtain a sample for feed moisture content (approximately 1 kg).
2. Screen the remainder (5 kg or more) on a 5-cm (2-in.) screen. Save −5 cm material for subsequent recombination with crushed +5-cm material.
3. After screening, weigh ±5-cm screened materials and calculate ±5-cm weight distributions.
4. Crush (may hand break) +5-cm material to just pass a 5-cm (2-in.) screen and recombine with the screened −5-cm material.
5. Thoroughly blend the recombined 100% −5-cm mine rock sample, and using the feed moisture content (step 1 above), calculate the dry weight of the sample to ensure that a minimum of 5 kg (dry weight) is available for the MWMP extraction (column percolation) test.
6. Load the 100% −5-cm mine rock sample into the extraction device (column) in a manner to minimize particle segregation and compaction.

Extraction Procedure

1. Adjust the extraction fluid application rate such that the number of milliliters of water applied to the column in a 24-h period will be equal to the number of dry grams of mine rock sample in the column.
2. Measure and record the initial pH of the extraction fluid.
3. Begin metering the extraction fluid onto the top of the mine rock contained in the column at the predetermined rate.
4. When a volume equal to the mass of dry solids in the column has been delivered through the column (assume 1 mL/g), cease application of the extraction fluid. *Note: The mine rock charge will retain water, so extraction fluid application must continue until the target effluent volume (1 : 1 solids to effluent ratio) has been collected. This will require application time beyond 24 h, but not to exceed 48 h.*
5. Thoroughly mix the effluent immediately. Then procure a sufficient quantity for the analyses required (usually, profile I or profile II).
6. Measure and record the pH of the extract.
7. Filter the sample through a 0.45-µm inert membrane to obtain an extract for dissolved constituent

analyses.

8. Preserve the extract sample appropriately for the analyses required.
9. Allow the mine rock solids, after extraction, to drain until the surface of the sample no longer “glistens” and allow at least 2 min to elapse between drops of effluent from the column.
10. Remove the mine rock residue (solids) from the column and take a representative portion for residual moisture determination.
11. Blend and split the moist mine rock residue to obtain samples for additional analysis if necessary.
12. If it is evident at step 3 that the particle size of the sample (finely divided solids such as clayey soils, sludges, mill tailings, etc.) is not allowing reasonable percolation of the extraction fluid to occur, aborting the extraction procedure and submitting the sample to an alternative extraction procedure may be advised.

Reporting

Record and report the following to the Nevada Department of Environmental Protection.

1. pH of extraction fluid (influent).
2. pH of effluent after extraction.
3. Total dry weight of mine rock sample used for MWMP.
4. Fed and retained (after extraction and draining) moisture content.
5. Time of contact in the extraction device.
6. Procedures (synopsis) used for MWMP extraction, effluent filtration, and extract preservation.
7. Results of profile I or profile II analyses on extract.

Notes

1. Standard Methods for the Examination of Water and Wastewater, 18th ed., APHA/AWWA/WEF, 1992, Method 1080. Based on data collected for wet depositions in Nevada, obtained from the Desert Research Institute, University of Nevada System, type II reagent-grade water most closely simulates meteoric water in Nevada in terms of both composition and pH range. Personal communication of M.N. Shen with Rick Stone, June 1995.
2. The extraction fluid can be metered via variable-speed delivery devices such as peristaltic pumps or diaphragm pumps. A constant hydraulic head device can be used wherein a single-speed pump delivers the extraction fluid to an elevated vessel that is equipped with an overflow back to the extraction fluid reservoir. The constant-head vessel is tapped at the bottom to supply extraction fluid to the extraction column. A variable pinch clamp or screw clamp can be used to control the rate of extraction fluid application to the column.
3. The effluent container can be calibrated so as to overflow after the desired volume of extract has been collected. For example, if a 5-kg charge of solids is used, a 5-L vacuum flask can be used as a receiver. Sufficient inert glass beads can be added to the vessel to cause overflow when 5 L of extract has been received. Therefore, a technician need not be available at the exact time the target effluent volume has been achieved.

4. If the effluent contains finely divided suspended matter, filtration may be difficult. It is suggested that in such cases filtration through a 0.45-µm membrane be preceded by centrifugation and/or prefiltration using a larger-pore glass fiber filter.
5. An aliquot for metals analysis must be preserved with reagent-grade nitric acid to pH < 2. An aliquot for phosphorus and nitrate analysis must be preserved with reagent-grade sulfuric acid to pH < 2. An aliquot for cyanide analysis must be preserved with reagent-grade sodium hydroxide to pH > 12. All other analyses reported in profiles I and II require only that the sample be stored without preservative at 4 ± 2°C.
6. Residual moisture (RM) can be determined by placing a representative portion of the moist mine rock residue (following step 9) into a preweighed beaker or similar vessel. The sample is then placed in an oven controlled at 105 ± 2°C overnight, or until the difference between weighings at 30-min heating intervals is less than 0.1%. The difference between the wet and dry weights multiplied by 100, yields the percent residual moisture: [(wet wt – dry wt) ÷ dry wt] × 100 = %RM.

Reference

Nevada Mining Association, 1996. Meteoric Water Mobility Procedure (MWMP), Standardized Column Percolation Test Procedure. Nevada Mining Association, Reno, NV, 5 pp.

British Columbia Special Waste Extraction Procedure: Leachate Extraction Procedure

This is the full version of the British Columbia Special Waste Extraction Procedure as detailed in the BC Waste Management Act. It was developed specifically for special wastes, not for materials tested in ABA work, and the leaching solution is acetic acid. For ABA work it is standard practice in British Columbia to use distilled water or 0.1 N hydrochloric acid as the extractant (Price, 1997; Price et al., 1997) at a 3 : 1 liquid/solid ratio and an extraction time of 24 h.

Sampling

1. For wastes with 0.5% solids weight by volume or greater, collect a sufficient amount of sample to provide approximately 100 g of solid material using techniques which ensure that the sample is representative of the waste.
2. If the waste has less than 0.5% solids weight by volume, collect at least 1 L of sample.

Equipment

1. Sieve, 9.5-mm mesh opening, stainless steel or plastic material.
2. Stainless steel filtration unit, 142 mm in diameter, minimum 1 L capacity, capable of sustaining a pressure of 5 kg/cm^2, applied to the material to be filtered.
3. Membrane filter 142 mm in diameter, pore size of 0.45 µm diameter, made of synthetic organic material such as cellulose acetate, cellulose nitrate, nylon, or polycarbonate that is compatible with the leachate to be filtered. Teflon is recommended for organic constituents.
4. Glass fiber prefilter 124 mm in diameter with a pore-size range of 3 to 12 µm.

5. Vacuum filtration unit 90 mm in diameter.
6. Membrane filter 90 mm in diameter (see step 3).
7. Glass fiber filter 70 mm in diameter (see step 4).
8. Solid-waste rotary extractor—a device that rotates the bottles end over end about a central axis through 360° at a speed of 10 rpm. The dimensions of the box will depend on the needs of each laboratory.
9. Structural integrity tester with a 3.18-cm-diameter hammer weighing 0.33 kg and having a free fall of 15.24 cm.
10. pH meter with a readability of 0.01 pH unit and an accuracy of ±0.1 pH unit.
11. Cylindrical bottles, wide mouth, 1250 mL capacity, polyethylene or glass with Teflon-lined cap for inorganic constituents; glass with Teflon-lined cap or Teflon bottles for organic constituents.
12. All glassware and equipment that comes into contact with the sample should be cleaned in the following way before each use:
    a. Wash with a nonphosphate detergent solution.
    b. Rinse twice with tap water.
    c. Rinse twice with reagent water.
    d. Wash with 10% nitric acids.
    e. Rinse several times with reagent water.
    f. Store bottles filled with 10% nitric acids until ready to use.
    g. Rinse several times with reagent water before use.
    h. Rinse clean oven-dried bottles with methylene chloride, followed by methanol, for organic constituents.

Reagents

1. Acetic acid, 0.5 N. Dilute 29.4 mL of concentrated acetic acids (ACS grade) to 1000 mL with reagent water.
2. Reagent water, type IV (ASTM Specification D1193). For organic parameters, the reagent water should be free of any organic substances to be analyzed (ASTM type 1).
3. Nitric acid, 10% v/v. Add 100 mL of concentrated nitric acid (ACS grade) to 900 mL of reagent water.
4. Nitrogen gas, prepurified, scrubbed through a molecular sieve.

Separation Procedure

If the sample is not a dry solid, separate it into its component phases using the following procedure:

1. Determine the dry weight of the solids in the sample at 60°C using a well-homogenized sample. Use this weight to determine the amount of material to be filtered.
2. Assemble the filtration unit with a filter bed consisting of a 0.45-µm-pore-size membrane filter and a

coarse-glass-fiber prefilter upstream of the membrane filter (per the manufacturer's instructions).

3. Select one or more blank filters from each batch of filters. Filter 50-mL portions of reagent water through each test filter and analyze the filtrate for the analytical parameters of interest. Note the volume required to reduce the blank values to acceptable levels.
4. Wash each filter used in the leach procedure with at least this predetermined volume of water. Filter under pressure until no water flows through the filtrate outlet.
5. Remove the moist filter bed from the filtration unit and determine its weight to the nearest ±0.01 g.
6. Reassemble the filtration unit, replacing the filter beds, as before.
7. Comminute the sample with a mortar and pestle to a size that will pass through the opening of the filtration unit (less than 9.5 mm).
8. Agitate the sample by hand and pour a representative aliquot part of the solid and liquid phases into the opening of the filtration unit. Filter a sufficient amount of the sample to provide at least 60 g of dry solid material.
9. Pressurize the reservoir very slowly with nitrogen gas by means of the regulating valve on the nitrogen gas cylinder until liquid begins to flow freely from the filtrate outlet.
10. Increase the pressure in increments of 0.5 kg/cm^2 to a maximum of 5 kg/cm^2 as the flow diminishes. Continue filtration until the liquid flow ceases or the pressurizing gas begins to exit from the filtrate outlet of the filter unit.
11. Depressurize the filtration unit slowly using the release valve on the filtration unit. Remove and weigh the solid material together with the filter bed to ±0.01 g. Record the weight of the solid material.
12. Measure and record the volume and pH of the liquid phase. Store the liquid at 4°C under nitrogen until required in step 13 of the extraction procedure.
13. Discard the solid portion if the weight is less than 0.5% w/v of the aliquot part taken and proceed to step 14 of the extraction procedure. If not, proceed to Step 1.

Note: For mixtures containing coarse-grained solids, where separation can be performed without imposing a -5 kg/cm^2 differential pressure, a vacuum filtration unit with a filter bed as in step 2 may be used. Vacuum filtration must not be used if volatile organic compounds are to be analyzed.

Extraction Procedure

1. Prepare a solid sample for extraction, by crushing, cutting, or grinding, to pass through a 9.5-mm mesh sieve. if the original sample contains both liquid and solid phases, use the solid material from step 13 of the separation procedure. The structural integrity procedure, step 6, should be used for monolithic wastes that are expected to maintain their structural integrity in a landfill (e.g., some slags and treated solidified wastes).

   Note: Do not allow the solid waste material to dry prior to the extraction step.
2. Determine the moisture content of the dewatered sample by drying a suitable aliquot part to a constant weight at 60°C in an oven. Discard the dried solid material.
3. Place the equivalent of 50 g dry weight of the dewatered undried material into a 1250-mL wide-mouth cylindrical bottle. Use additional bottles if a larger volume of leachate is required for the analysis.
4. Add 800 mL (less the moisture content of the sample in milliliters) of reagent water to the bottle.

5. Cap the bottle and agitate it in the rotary extractor for 15 min before pH measurement.
6. Measure and record the pH of the solution in the bottle using a pH meter calibrated with buffers at pH 7.00 and 4.00. The solution should be stirred during the pH measurement.
7. If the pH is less than 5.2, proceed to step 10.
8. If the pH is greater than 5.2, add a sufficient volume of 0.5 N acetic acid to bring the pH to 5.0 ± 0.2. If the pH is not lowered to 5.0 ± 0.2 with this amount, proceed with the extraction.
   Note: No more than 4 mL of 0.5 N acetic acid per gram of dry weight of sample may be added during the entire procedure.
9. Cap the bottle and place it in the tumbling apparatus. Rotate the bottle and its contents at 10 rpm for 24 h at room temperature (20° to 25°C).
10. Monitor and manually adjust the pH during the course of the extraction if it is greater than 5.0 ± 0.2. The following procedure should be followed carefully.
    a. Measure the pH of the solution after 1, 3, and 6 h from the starting time. If the pH is above 5.2, reduce it to pH 5.0 ± 0.2 by addition of 0.5 N acetic acid. If the pH is below 5.0 ± 0.2, do not make any adjustments.
    b. Adjust the volume of the solution to 1000 mL with reagent water if the pH is below 5.0 ± 0.2 after 6 h.
    c. If required, measure and reduce the pH to 5.0 ± 0.2 after 22 h, and continue the extraction for an additional 2 h.
11. Add enough reagent water at the end of the extraction period so that the total volume of liquid is 1000 mL. Record the amount of acid added and the final pH of the solution.
12. Separate the material into its component liquid and solid phases as described under the separation procedure, step 4. Discard the solid portion.
    Note: It may be necessary to centrifuge the suspension at high speed before filtration for leachates containing very fine-grained particles.
13. Calculate the amount of free liquid from step 12 of the separation procedure, corresponding to 50 g of the dry solid material. Add this amount to the leachate from step 12 above.
    Note: If the analysis is not performed immediately, store separate aliquot parts of the leachate at 4°C, after adding appropriate preservatives for the analytical parameters of interest.
14. If the weight of the solid portion in step 1 was less than 0.5% w/v, analyze the free liquid from step 13 of the separation procedure; otherwise, analyze the combined solutions from step 13 above for contaminants that are likely to be present.
15. Report concentrations of contaminants in the combined leachate and the free liquid solution as mg/L.
16. Carry a blank sample through the entire procedure, using dilute acetic acid at pH 5.0 ± 0.2.

Structural Integrity Procedure

1. This procedure may be required prior to extraction for some samples as indicated in step 1 of the extraction procedure. It may be omitted for wastes with known high structural integrity.
2. Fill the sample holder with the material to be tested. If the sample of the waste is a large monolithic block, cut a portion from the block measuring 3.3 cm in diameter by 7.1 cm in length. For a treated

waste (e.g., solidified waste) samples may be cast in a form with the dimensions above for the purposes of conducting this test. In such cases, the waste should be allowed to cure for 30 days prior to further testing.

3. Place the sample holder in the structural integrity tester, then raise the hammer to its maximum height and allow it to fall. Repeat this procedure 14 times.
4. Remove the material from the sample holder and proceed to step 2 of the extraction procedure. If the sample has not disintegrated, it may be sectioned; alternatively, use the entire sample (after weighing) and a sufficiently large bottle as the extraction vessel. The volume of reagent water to be added initially is 16 mL/g of dry sample weight. The maximum amount of 0.5 N acetic acid to be added is 4 mL/g of dry sample weight. The final volume of the leachate should be 20 mL/g of dry sample weight.

Reference

Province of British Columbia, 1992. Waste Management Act: Special Waste Regulation Schedule 4, Parts 1 and 2. Queen's Printer, Victoria, BC, Canada, pp. 72–79.

British Columbia Special Waste Extraction Procedure: Modified Leachate Extraction Procedure

The modified leachate extraction procedure is identical to the leachate extraction procedure except that:

- Sections 1 to 4 inclusive of the reagents list are deleted and replaced by:
  1. Reagent water, type IV (ASTM specification D1193)
  2. Nitrogen gas, prepurified, scrubbed through a molecular sieve.
- Steps 5 to 11 inclusive of the extraction procedure are deleted and replaced by:
  5. Cap the bottle and agitate it in the rotary extractor for 1 h.
  6. Add enough reagent water at the end of the extraction period so that the total volume of liquid is 1000 mL.
- Step 16 of the extraction procedure is deleted.

Reference

Province of British Columbia, 1992. Waste Management Act: Special Waste Regulation Schedule 4, Parts 1 and 2. Queen's Printer, Victoria, BC, Canada, pp. 72–79.

U.S. Environmental Protection Agency: Synthetic Precipitation Leaching Procedure and Toxicity Characteristic Leaching Procedure

As with the British Columbia Special Waste Extraction Procedure (SWEP) described above, the synthetic precipitation leaching procedure (SPLP) and the toxicity characteristic leaching procedure (TCLP) were developed for use in the assessment of waste disposal facilities rather than mining operations. The TCLP (U.S. EPA Method 1311) evaluates metal mobility in a sanitary landfill, and the SPLP (U.S. EPA Method

1312) was developed to evaluate the fate and transport of metals in an engineered land disposal facility from which municipal solid waste is excluded (Alforque, 1996).

The extraction fluid for the TCLP is a buffered organic acid (acetic acid), while that for the SPLP is an aqueous solution (of sulfuric and nitric acids) intended to simulate rainwater. Consequently, the SPLP is likely to have higher suitability than the TCLP for use in ARD test work. Both procedures are described in U.S. EPA publication SW-846.

Reference

U.S. Environmental Protection Agency, 1996. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846. U.S. EPA, Washington, DC.

American Society For Testing And Materials: Shake Extraction Of Solid Waste With Water

ASTM D3987-85 is an ASTM procedure for the leaching of solid waste that consists of the shaking a known weight of waste with water of specified composition and separation of the aqueous phase for analysis. As with other procedures described above, this method was not developed specifically for use in the mining industry. It is probable that variations and modifications of the standard designated have been developed by those working in metal leaching and ARD prediction, such as the example given below.

Reference

American Society for Testing and Materials, 1992. Standard Test Method for Shake Extraction of Solid Waste with Water. ASTM Designation D3987-85. ASTM International, West Conshohocken, PA, 4 pp.

American Society for Testing and Materials: Modified ASTM Test D3987 For Shake Extraction Of Solid Waste With Water

This modification was supplied by an unnamed Canadian laboratory.

Materials

1. Dilution water is to be water specified in ASTM D3987, adjusted to pH 5.5 by carbonic acid addition immediately prior to use.
2. Tailings solids must be representative of the project material.

Apparatus

1. An agitator may be of any type that meets the general requirement in ASTM D3957.
2. Containers for agitating slurry may be of any size compatible with the agitator apparatus and must be clean, new, acid washed, and rinsed before use.

Procedure

1. Prior to selecting tailing solids for the procedure, they should be well mixed and free of lumps or standing water. The material must be kept in pails, firmly closed when not in use and stored in a cool location.
2. Immediately after selection, for a weighed quantity of well-mixed tailings material, calculate the dry weight of solids and the weight of associated water from the given solids content.
3. Add sufficient freshly prepared dilution water to give a 4 : 1 liquid/solid ratio (a solids content of 20 wt%):

$$\frac{\text{dry weight of solids in slurry}}{\text{water in slurry} + \text{water added}} \times 100 = 20\%$$

   Sufficient material should be prepared to almost fill the containers to be placed on the agitator.
4. Place the containers on the agitator apparatus and run for 18 h.
5. After completion of the agitation, remove the surface water by decantation followed by pressure filtration or centrifugation (good water recovery is essential).
6. Store all the water recovered without preservation or filtration in a single large clean carboy or add equal proportions of each new batch or aqueous solution generated to all leachate storage containers used. Where preservation is required for analysis, representative subsamples should be taken and suitably treated and labeled.

References

American Society for Testing and Materials, 1992. Standard Test Method for Shake Extraction of Solid Waste with Water. ASTM Designation D3987-85. ASTM International, West Conshohocken, PA, 4 pp.

Nevada Mining Association, 1996. Meteoric Water Mobility Procedure (MWMP), Standardized Column Percolation Test Procedure. Nevada Mining Association, Reno, NV, 5 pp.

Page, A.L., Miller, R.H., and Keeney, D.R., 1982. Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, 2nd ed., American Society of Agronomy and Soil Science Society of America, Madison, WI, pp. 199–209.

Price, W.A., 1997. Draft: Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia. British Columbia Ministry of Employment and Investment, Energy and Minerals Division, Smithers, BC, Canada, 143 pp.

Price, W.A., and Errington, J.C., 1995. ARD Guidelines for Mine Sites in British Columbia. British Columbia Ministry of Energy, Mines and Petroleum Resources, Victoria, BC, Canada, 29 pp.

Price, W.A., and Kwong, Y.T.J., 1997. Waste rock weathering, sampling and analysis: observations from the British Columbia Ministry of Employment and Investment database. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 31–45.

Price, W.A., Morin, K., and Hutt, N., 1997. Guidelines for the prediction of acid rock drainage and metal leaching for mines in British Columbia, Part II, Recommended procedures for static and kinetic testing. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 15–30.

Province of British Columbia, 1992. Waste Management Act: Special Waste Regulation Schedule 4, Parts 1 and 2. Queen's Printer, Victoria, BC, Canada, pp. 72–79.

Sobek, A.A., Schuller, W.A., Freeman, J.R., and Smith, R.M., 1978. Field and Laboratory Methods Applicable to Overburden and Minesoils. EPA-600/2-78-054, U.S. National Technical Information Service Report PB-280 495. U.S. EPA, Washington, DC.

U.S. Environmental Protection Agency, 1996. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846. U.S. EPA, Washington, DC.

Particle Size and Acid Liberation Evaluation

In kinetic ARD test work as in field behavior, particle size, particle-size distribution, and individual mineral grain size are parameters that affect both acid generation and acid neutralization. For pyrite and pyrrhotite grains to oxidize, there must be exposure of these grains to the atmosphere. For neutralizing mineral grains to react with acid produced, such grains must be exposed to the acid. The degree to which individual grains are exposed depends to a great extent on the size of the individual grains relative to the size of the rock sample in which they are contained.

In most of the world, it has been standard practice for many years to use ISO Standards for screening analysis. These standards use square aperture size (in millimeters or micrometers) for standard screening analysis rather than the “mesh sizes” formerly used by various national organizations and used currently in the United States under ASTM standards. Current practice prefers or requires (depending on regulatory authority) the use of SI (Système Internationale) units. The mesh size is dependent on the weave of screen cloth (i.e., wire diameter and spacing of the screen wires). Most mesh series were originally based on either the fourth root of the integer 2 or the square root of the integer 2, and on available wire size and weaving techniques. The ISO standards maintain this basis but use absolute dimensions to normalize individual national standards.

Unlike ABA procedures, where samples are finely ground (100% −75, −45, or −38 μm), samples for kinetic test work may have significant size ranges. For example, for the ASTM humidity cell procedure the sample should be 100% passing 6.3 mm (1/4 in.), while column tests are commonly run on material less than about 25 mm, and lysimeters may be operated with run-of-mine material that may be as coarse as 500 mm or greater. Although a specified mass may be used for a kinetic test (e.g., 1 kg for the ASTM humidity cell procedure), the sample specific surface area (usually expressed in m^2/kg) depends on the sample particle size distribution, and the mineralogical characteristics of the sample. Because of these dependencies, two concepts from the mineral processing field must be introduced into ARD prediction: (1) particle size distribution, and (2) mineral liberation size (liberation size determination and surface sulfur determination methods).

Particle Size Distribution

When rocks are broken (by blasting, crushing, or grinding), particles are produced with a continuous size distribution from the coarsest particle in the product to the finest (which is theoretically a particle of zero size). The continuity of this particle size distribution may be broken when the fragmented material is subjected to an imposed process such as screening or hydraulic classification—in which case any products of the process will have their own unique size distribution that will differ from that of the original material. Many methods, of varying complexity, have been developed to quantify the size distribution of particulates (Lynch, 1977; Bond, ; Lynch and Lees, 1985). One relatively uncomplicated

method that has found favor in the North American metalliferous mining industry since 1940 is the Gates–Gaudin–Schuhmann equation:

$$y = \left(\frac{x}{k}\right)^m$$

where y is the fraction of the sample finer than size x, and k (size modulus) and m (distribution modulus) are constants for the particular distribution. If the logarithm of the cumulative percent weight passing size x is plotted against the logarithm of particle size x, a relatively straight line is often obtained, with a slope equal to m and an intercept at 100% cumulative weight passing of k. The size distribution is therefore characterized by two simple parameters, k and m. For any given group of size distributions, the higher the value of k, the coarser the size distribution, and the higher the value of m, the narrower the size distribution (and vice versa). For a fixed mass of sample and value of k, specific surface area increases as the width of the size distribution increases (i.e., as m decreases).

Figure 20.3 shows Gaudin–Schuhmann size distributions for eight samples of a crushed drill core from the same deposit prepared for humidity cell test work by the same method. All of the curves appear to converge at a 100% cumulative percent weight passing size of about 16 mm (5/8 in.); thus, the value of k for all samples is 16 mm or 16,000 µm. The slopes, or gradients, of the curves range from approximately 0.5 for sample 5 to approximately 1.1 for sample 4, although the curves for samples 4, 6, and 7 cannot be described as a straight line. The eight samples thus have a range of values for m, from 0.5 to 1.1, and sample 5 has the widest, and sample 4 the narrowest, size distributions. Sample 4 would be expected to have the least specific surface area, and sample 5, the greatest.

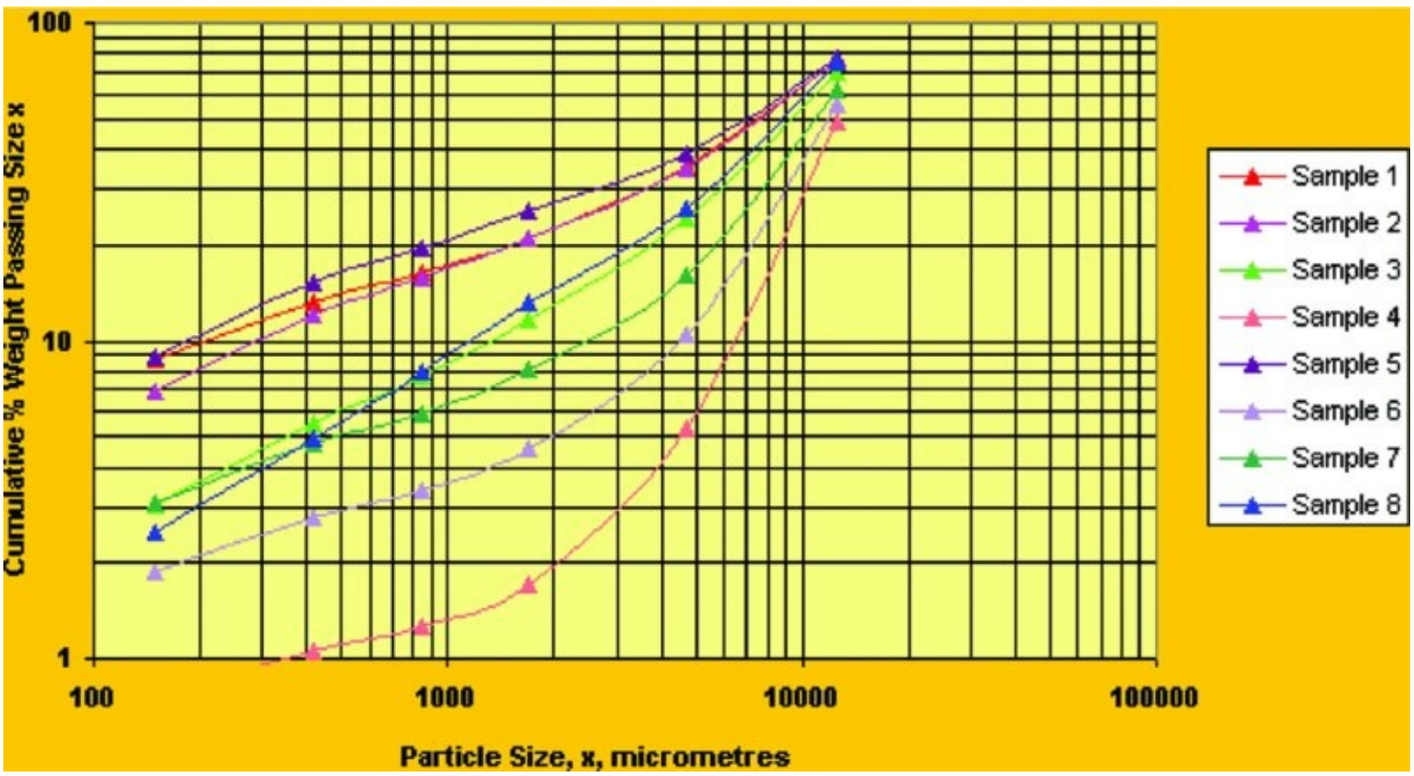

Figure 20.3 Gaudin–Scuhmann size distributions for eight humidity cell samples. (The data source is confidential.)

A characteristic that is of considerably more use in the interpretation of ARD test work than simple particle size distributions is an estimate of sample total or specific surface area. For the eight samples

above, these estimates have been made, assuming all particles to be spherical with a maximum particle size (*k*) of 16 mm and a minimum particle size of 2 µm (chosen as probably being the finest-sized particle retained in an operational humidity cell, and introducing into calculations less than a 1% error). Since testing screens are manufactured with apertures in series based on the fourth root of 2, the geometric mean of the upper and lower screen size for each fraction should be used as a mean fraction particle size rather than an arithmetic mean. Table 20.5 shows the specific surface area calculated (m^2/kg) and the percentage of the total sample surface area contributed by the finest (−150 + 2 µm) fraction of the sample for the eight samples.

Table 20.5 Calculated Specific Surface and Percentage of Total Surface Area Contributed by −150 + 2 µm Fractions for Data in Figure 20.3

Sample Number	Calculated Specific Surface (m^2/kg)	Percentage of Total Surface Area Contributed by −150 + 2 µm Fraction
1	12.0	93.2
2	9.77	90.8
3	4.51	86.4
4	1.28	79.1
5	12.5	92.0
6	2.75	86.9
7	4.42	89.6
8	3.86	82.7

The specific surface area calculated for the samples ranges from 1.28 (sample 4) to 12.5 (sample 5) m^2/kg, which represents a range of almost an order of magnitude. In general, the specific surface area values correlate well with the size distribution curves, in that the wider the size distribution, the greater the specific surface area.

A difference of an order of magnitude between the specific surface area of humidity cell samples from the same location and prepared in a similar manner is significant. To be of any validity, comparisons between the results of humidity cell test work on these eight samples would need to be on a normalized surface area basis, not on a mass basis. The variation between the percentage of surface area contributed by the −150 + 2 µm fractions is from 79.1% (sample 4) to 93.2% (sample 1), and this is also significant, representing an absolute difference of 14.1%.

The specific surface area of particles is proportional to the reciprocal of their size as shown in Figure 20.4 for spherical particles. The points on the graph correspond to the geometric mean particle size for each size fraction in the example above: 14.1 mm, 7.7 mm, 3.1 mm, 1.3 mm, 652 µm, 274 µm, and 17 µm. The range of specific surface area values for these mean particle sizes is from 0.16 to 129 m^2kg.

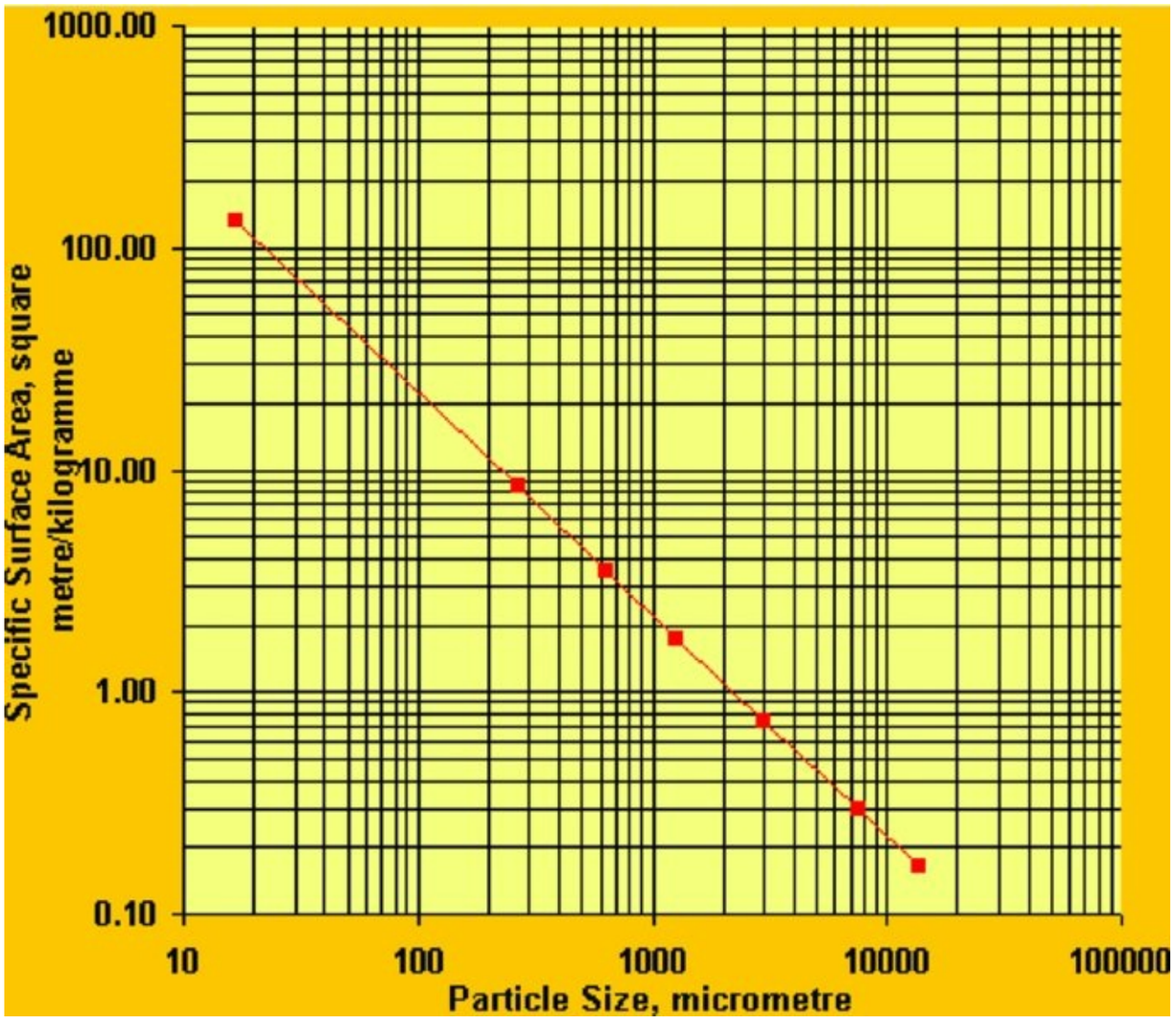

Figure 20.4 Specific surface area versus size for spheres.

If fine-size particle size distribution is critical in an evaluation of kinetic ARD tests, a more rigorous size-distribution determination procedure than the one used above should be employed. This should include dry screening at 105, 75, and 44 or 37 µm, wet screening at 44 or 37 µm, and cyclosizing. A Warman cyclosizer (a commonly used item in mineral processing laboratories, and shown in Figure 20.5) typically gives size splits for material with a relative density of 2.7 of 44, 29, 19, 14, and 11 µm. Further refinements to specific surface area determination can be made by determining the particle shape factor for each size fraction and applying this to the spherical particle approximation.

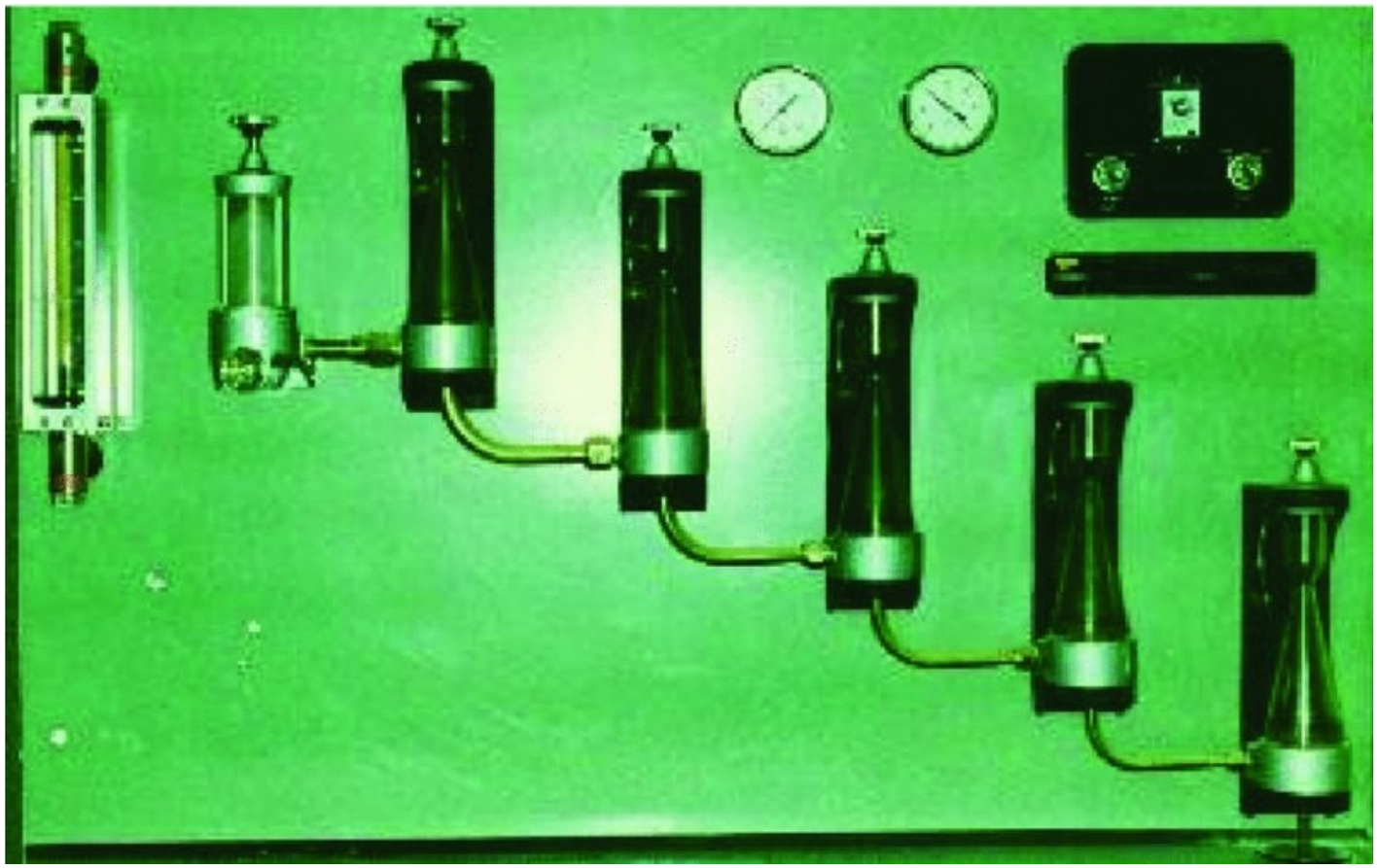

Figure 20.5 Warman cyclosizer.

Mineral Liberation Size

The textural relationships between minerals within an ore, and their relation to process selection, requires introduction of the concept of liberation size. This is the size to which an ore must be crushed or ground to produce separate particles of either value mineral or gangue that can be removed from the ore (as concentrate or tailings) with an acceptable efficiency by a commercial unit process. Liberation size does not imply pure mineral species but, rather, an economic trade-off of grade and recovery. The concept of liberation and liberation size may be extended to ARD prediction, where atmospheric leaching becomes the relevant unit process. Atmospheric pyrite and pyrrhotite oxidation requires that part of the mineral grain be exposed or liberated with respect to leaching. For any given pyritic or pyrrhotitic rock, the degree of pyrite or pyrrhotite mineral grain exposure increases with decreasing particle size, attaining 100% exposure or liberation with respect to leaching when all of the rock has been reduced in size to that of the smallest grain of pyrite or pyrrhotite. It is usually only at 100% exposure or liberation that acid generation potential determined by ABA (static) methods equals the acid generation potential of kinetic test or field samples.

Thus, grains of pyrite or pyrrhotite in whole rock will have less exposure (less liberation) than those in blasted waste rock, and those in blasted waste rock will have less exposure (less liberation) than those in mill tailings. Size reduction corresponds to an increase in total particle surface area. Particle specific surface area is proportional to the reciprocal of particle size.

Figure 20.6 shows four possible scenarios for pyrite, pyrrhotite, or metallic sulfide mineral liberation from nonsulfide minerals such as silicates, oxides, and carbonates. The particles are shown in section view as they would be seen when sawed through for macroscopic examination or microscopic viewing in

transmitted or reflected light. Both the first and fourth particles contain a sulfide mineral grain that is liberated with respect to atmospheric leaching. The second and third particles contain a grain or grains of a sulfide mineral that are not liberated with respect to atmospheric leaching. It is quite possible for all four grains to have the same sulfide-sulfur analysis, and thus the same AP, and to have the same NP. In this case, ABA (static) analysis would rate the four grains equally with respect to potential ARD generation. However, in a kinetic test only particles 1 and 4 would have the potential to generate acid, as they would in the field.

Figure 20.6 Four possible scenarios for pyrite or pyrrhotite liberation.

Liberation size can be estimated from petrographic studies, especially the microscopic examination of thin and polished sections. Liberation size can also be determined by quantitative mineralogical test work on size fractions of ground ore, although this is considerably less common because it is costly, time consuming, and often technically difficult. However, for the determination of potential ARD generation problems with tailings, the methodology produces information that simple chemical analysis does not.

Liberation size is a function of the relevant physical or chemical process and may differ greatly between processes (Mills, 1995). Since ARD generation is a sulfide (pyrite) leaching process and base metal concentration is usually by flotation from gangue sulfide (pyrite), these differences may have significance in ARD prediction. The liberation size of pyrite for both flotation and leaching (and gravity concentration if it is included in the mill flowsheet) is therefore a most important parameter. This information is extremely difficult to determine without quantitative mineralogical studies. Size reduction for liberation

naturally produces a size range of particles. This range is dependent on the type of size reduction method used, and the hardness, texture, friability, and degree of weathering of the rock and its constituent minerals.

For ARD prediction the important characteristics of ore or waste are:

1. The amount of pyrite and/or pyrrhotite in the ore or waste.
2. The degree of pyrite and/or pyrrhotite liberation produced by size reduction with respect to potential oxidation and leaching.
3. The presence of, and association with pyrite of, trace metal sulfides.
4. The amounts of leachable metallic sulfide minerals in the ore or waste.
5. The degree of liberation of leachable metallic sulfide mineral produced by size reduction with respect to leaching.

Most of the mineralogical test work conducted in the field of ARD has focused on the products of pyrite oxidation and the products of ARD neutralization within tailings impoundments. It is considerably easier to determine particle size distribution and liberation characteristics for tailings than it is for waste rock dumps. For existing tailings, size distribution may be representatively determined from testing screen results, while liberation characteristics may usually be obtained using visible-light microscopic techniques. For existing waste rock dumps, the acquisition of representative size distributions is very difficult since the particle size ranges from the coarsest material produced by blasting to the finest material retained after rain and snow infiltration and flushing. Liberation characteristics for waste dump material may be (and usually are) inferred from examination of the finer dump material. Where only drill core is available, liberation characteristics can be determined by microscopy techniques, but estimated size distributions require information on the proposed mining method and milling flowsheet. Metallurgical test work is usually conducted concurrently with ARD test work, so that tailings from test work programs are normally available for ARD study.

It is particularly important that metallurgical and ARD test work be integrated because a well-designed mill will not only optimize metallurgical performance, but also minimize potential ARD problems. A good recent example of this integration is demonstrated by the design of the proposed Tulsequah Chief mine in British Columbia as reported by Rescan Environmental Services Ltd. (1997). In the proposed Tulsequah Chief mill, pyrite will be concentrated by froth flotation following base metal sulfide concentration and recovery. The pyrite concentrate will be deposited subaqueously in the underground mine. The mill tailings, containing some residual pyrite and potentially acid generating, will be blended with ground limestone for subaqueous deposition in the tailings impoundment for the operational life of the mine. At mine closure the tailings impoundment will be allowed to drain and the tailings will progress to subaerial storage. Mill design with respect to mineralogy and potential ARD generation was examined by Mills (1995) for the Huckleberry mine in British Columbia.

The effect of particle size on some ARD static procedure measured values for waste rock dumps at four sites in British Columbia has been reported by Price and Kwong (1997). In all cases only −100-mm material was examined and samples were taken only from the top 1 m of the dump. Sized fractions, −100 + 19 mm, −19 + 11 mm, −11 + 2 mm, −2 mm + 50 μm, and −50 μm, were subjected to paste pH, carbonate NP, Sobek NP, and sulfide-sulfur determinations. Although the results show variations in the values of these measured quantities with particle size, the authors concluded only that ``The data provided illustrates: differences in the composition of different particle size fractions, the inadequacy of a whole sample assay as a means of characterizing weathering, and the importance of separately analysing a fine

particle size fraction (< 2 mm) when evaluating weathering effects".

The static procedures used in this test work all require that a sample be pulverized, so liberation characteristics of acid-generating minerals and neutralizing minerals could not be observed. In a waste rock pile a size fraction of −2 mm would be expected to have a relatively high degree of liberation of both acid-generating and acid-neutralizing minerals when compared to the coarser fractions. As a result, it would be expected that in situ acid generation and neutralization had occurred with a concurrent reduction in carbonate NP, Sobek NP, and sulfide sulfur (AP) compared to the coarser fractions. Other causes of differences between size fractions may be mineralogical in nature: for example, the friability of pyrite relative to calcite can produce more fine pyrite particles of a given size than calcite particles of the same size after size reduction by impact.

Price and Kwong (1997) note that the −2-mm fraction of their samples represented 10 to 30% of the sample mass. Price (1997) notes that most laboratory (i.e. static) analyses do not distinguish between liberated and unliberated mineral species and recommends that in the absence of site-specific data (liberation size studies) that indicate otherwise, the −2-mm fraction of waste rock should be considered the reactive fraction in ARD prediction studies. He gives the following potentially negative effects of such an approach:

- Sieving is required, and additional handling could alter the quality of the sample.
- A large enough subsample of the −2-mm fraction may be unavailable, and too small a sample size may not yield representative data.
- The analysis will not measure the contribution from the coarse fragments, which may be significant if coarse fragments are incompetent or porous, or the −2-mm fraction is unreactive.
- The analysis assumes that most contaminant release comes from this size fraction. This assumption may not be correct for historic mine wastes and for naturally weathered materials in which weathering has progressively removed reactive minerals from the finer particles.

In western Canada, a widely used approximation for the reactive portion of waste rock dumps is 10 to 20%, based on observations of the magnitude of the −2-mm weight fraction of waste rock dumps. Price and Kwong (1997) reported a range of 10 to 30% −2 mm for their −100-mm waste dump samples, and Murray (1977) has given an average of 15 to 25% with a range of 0 to 35% for waste rock at Canadian precious and base metal mines.

The approximations and practices above notwithstanding, ARD programs should include liberation studies in all but the most straightforward cases, and particularly in cases where predictions from static and kinetic test work are inconsistent or contradictory.

Liberation Size Determination Methods

Low-power stereoscopic microscopy and high-power petrographic microscopy (particularly using dark-field illumination) are usually the most productive tools. It is often preferable to size (screen) and concentrate samples prior to examination. The concentration process will depend on the type and complexity of sample, but the aim is to identify the distribution and degree of liberation of pyrite, pyrrhotite, metallic sulfide minerals, and their mode of occurrence. Heavy liquids such as 1,1,2,2-tetrabromoethane, tri-iodomethane, and (less commonly) Clerici solution (Mills, 1978, 1985) have been used to concentrate the more dense fractions of mineral-bearing samples, giving a range of relative densities up to about 5 (hot Clerici solution). Because they can be used in centrifuges, heavy liquids may be used with particles as fine as 1 to 5 µm, and therefore offer great flexibility. This flexibility is offset by

cost and toxicity considerations. For particles coarser than about 200 µm, the Magstream 50 (Domenico et al.,) offers some advantages for density separation. This unit is simple to operate, has high sample throughput, uses nontoxic chemicals, and can operate at a continuous range of relative densities comparable to heavy liquids. Generally, any concentration of samples would be to aid microscopy, not to isolate or separate pure mineral samples. A very useful guide to the physical and chemical identification of mineral in granular form has been written by Jones and Fleming (1965).

Surface Sulfur Determination

Another method for the determination of exposed or liberated sulfide grains in particulate samples was developed by Acme Analytical Laboratories Ltd. of Vancouver in collaboration with Bruce Downing in 1996. This method, which has not seen widespread use and is currently under further development, utilizes a weak acid leach and leachate analysis for sulfur to determine the soluble sulfide of size fractions of crushed or ground rock. This “surface sulfur” procedure is intended to measure the proportion of contained sulfide minerals that are exposed at granular surfaces and are thus liberated with respect to atmospheric leaching. Any sulfidic grains occluded in the rock particles, while contributing to sample total sulfur, will not be reported by the surface sulfur procedure, and a value for liberated sulfides as a percentage of total sulfides may therefore be determined. In relation to ARD prediction, the procedure generates a percentage liberation value for the oxidizable sulfides in each size fraction of a fragmented sample. This procedure appears to have considerable potential use in ARD prediction. However, this method was not fully developed beyond the concept stage and thus not implemented as a test procedure.

Summary

It is not unusual for kinetic ARD test work to produce results that are inconsistent with ABA results. This can usually be attributed to the fact that ABA tests measure total sulfides, whereas kinetic tests are dependent on exposed or liberated sulfides. As a consequence, kinetic tests may produce results which indicate that a sample is not net acid generating when ABA analysis has indicated that the sample is likely to be net acid generating. This situation arises most often when sulfides such as pyrite and pyrrhotite occur as inclusions finer than 5 µm in size as well as in the form of much coarser grains. In such conditions, the kinetic test has more validity than the ABA test, since the coarser material of a waste rock pile will also contain much unliberated sulfide. It is also possible for the situation to be reversed, in that some neutralization potential measured in ABA tests may not be realized in kinetic tests or in the field because the neutralizing minerals are not adequately liberated. In such cases a sulfide and/or neutralizing mineral liberation study would generally clarify inconsistencies.

The generation and neutralization of acid in waste rock piles, tailings, and exposed rock and ore in underground mines is surface-area, not mass, dependent. The example given above shows clearly that eight samples, from the same deposit and prepared in the same way for humidity cell tests, can vary by an order of magnitude in their specific surface area. In this particular case, metal-leaching rates based on mass rather than surface area, obtained from humidity cell tests, should not be compared directly with one another. Only when the metal-leaching rates are normalized with respect to surface area can comparisons be accepted as valid.

Acknowledgments

The basic material and concepts for this chapter were developed in part by the late Chris Mills, a mining engineer specializing in metallurgical engineering and surface chemistry. He was heavily involved as an

engineer in the mining industry throughout the world for over 30 years, and as a teacher and researcher he contributed many technical papers and classes on mining and acid rock drainage. Sadly, he died unexpectedly on February 10, 1999.

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References and Suggested Reading

American Society for Testing and Materials, 1996. Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell. Designation D5744-96. ASTM, International, West Conshohocken, PA, 13 pp.

Bond, F.C., 1985. Testing and Calculations.In: SME Mineral Processing Handbook, N.L. Weiss, ed. American Institute of Mining, Metallurgical and Petroleum Engineers, New York, vol. 3A, pp. 16–27.

Domenico, J.A., Stouffer, N.J., and Faye, C., 1994. Magstream as a heavy liquid separation alternative for mineral sands exploration. Presented at the Society of Mining Engineers Albuquerque Meeting, March, 14 pp.

Jones, M.P., and Fleming, M.G., 1965. Identification of Mineral Grains. Elsevier, London, 102 pp.

Lynch, A.J., 1977. Mineral Crushing and Grinding Circuits: Their Simulation, Optimization, Design and Control. Developments in Mineral Processing, vol. 1. Elsevier, Amsterdam, pp. 18–25.

Lynch, A.J., and Lees, M.J., 1985. Simulation and modeling. In: SME Mineral Processing Handbook, N.L. Weiss, ed. American Institute of Mining, Metallurgical and Petroleum Engineers, New York, vol. 3A, pp. 28–53.

Mills, C., 1978. Mineralogy and Heavy Liquid Analysis in Gravity Separation. Short Course on Gravity Concentration Technology. University of Nevada, Reno, NV, October, 25 pp.

Mills, C., 1985. Specific gravity fractionation and testing with heavy liquids. In: SME Mineral Processing Handbook. American Institute of Mining, Metallurgical and Petroleum Engineers, New York, vol. 30, pp. 44--52.

Mills, C., 1995. Technical Review of the Acid Rock Drainage (ARD) and Metal Leaching Aspects of the Metallurgical Test Work, Milling Practices and Tailings Monitoring for the Huckleberry Project. Report to the British Columbia Ministry of Energy, Mines and Petroleum Resources, October, 34 pp.

Murray, D.R., 1977. Pit Slope Manual Supplement 10-1. CANMET Report 77-31, Department of Energy, Mines and Resources Canada, Ottawa, ON, Canada.

Price, W.A., 1997. DRAFT Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia. British Columbia Ministry of Employment and Investment, Energy and Minerals Division, Smithers, BC, Canada, 143 pp.

Price, W.A., and Kwong, Y.T.J., 1997. Waste rock weathering, sampling and analysis: observations from the British Columbia Ministry of Employment and Investment database. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 31--45.

Rescan Environmental Services Ltd., 1997. Tulsequah Chief Project Report, Vol. II and IV. Rescan, Vancouver, BC, Canada.

21
Kinetic Testing Procedures

BRUCE W. DOWNING

Kinetic testing has been developed as a laboratory method to better predict the likelihood of acid drainage from potentially acid-generating rocks, sediments, and soils. The chapter includes descriptions of many historically important kinetic testing concepts and procedures. The U.S. Environmental Protection Agency developed Method 1627, Kinetic Test Procedure for the Prediction of Mine Drainage Quality, included in Appendix G (U.S. Environmental Protection Agency, 2001). Developments in humidity-cell tests and applications are discussed by Lapakko (2003).

Introduction

Acid–base accounting (ABA) procedures are used as a screening process to categorize materials into potentially acid-generating, potentially non-acid-generating, and uncertain groups. For material where the potential for acid generation is uncertain, kinetic test work is performed to attempt to define acid generation characteristics. The term *kinetic* is used to describe a group of test work procedures wherein the acid generation (and metal solubilization and transport) characteristics of a sample are measured with respect to time. ABA procedures are referred to as *static* because measurements are made over a short and fixed period of time. Procedures are described below for humidity cells, columns, and lysimeters, which are the three most commonly used methods of determining kinetic acid rock drainage (ARD) characteristics of drill core, waste and other rock samples, and tailings. A procedure for determining the kinetic ARD characteristics of in situ rock such as pit walls and the rock surfaces of adits, stopes, and other underground workings has been developed through the MEND Program and the British Columbia ARD Task Force. This procedure is called *minewall* (MEND, 1995). Humidity cells are typically laboratory units using a sample size of about 1 to 15 kg. Columns may be of laboratory, pilot plant, or site scale, with sample sizes ranging from a few to hundreds of kilograms. Lysimeters are site-scale units with sample sizes typically in the metric ton range. The minewall procedure has been used on exposed rock surfaces no greater than 1 m×1 m (Price, 1997). For an extensive review of kinetic geochemical processes and their relevance to the assessment of waste rock ARD potential, see Perkins et al. (1995).

All kinetic test work procedures contain the following elements:

- Subjection of sample to periodic leaching
- Collection of drainage for analysis
- Calculation of rates of acid generation and neutralization capability depletion
- Calculation of rates of metal release
- Prediction of water quality

As discussed below, calculated rates of acid generation, neutralization capability depletion, and metal release are for the test sample and equipment configuration and conditions used, and cannot be used directly for the prediction of field water quality (unless the sample is truly representative of its source material and field conditions are used, as would be the case with a large lysimeter test on site).

Humidity Cell and Column Test Work Equipment Arrangement

Figure 21.1 shows generic schematic diagrams for the arrangement of a humidity cell, a subaerial test work column, and one possible configuration for a subaqueous test work column. There are other possible configurations for subaqueous test work (Lawrence, 1995). Humidity cells have, in the past, varied considerably in dimensions. However, laboratories servicing the mining industry have now adopted a degree of standardization. In *ASTM Designation: D5744-96—Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell* (American Society for Testing and Materials, 1996), a cell 203 mm (8.0 in.) in height by 102 mm (4.0 in.) in diameter is specified for material crushed to 100% passing 6.3 mm (crushed core or waste rock, and coarse tailings), and a cell 102 mm (4.0 in.) in height by 203 mm (8.0 in.) in diameter is specified for material passing 150 µm (fine tailings). While recommending similar dimensions, Price (1997) states that the dry and humid airflow should be directed across the surface of tailings samples rather than through the samples from below. In both of the arrangements above, the sample mass is 1 kg, which typically gives a bed depth of about 80 to 120 mm in a 102-mm-diameter cell and 20 to 40 mm in a 203-mm-diameter cell, depending on sample bulk density. Soregaroli and Lawrence (1998) have reported the use of a 3-kg sample with a 102-mm-diameter cell and a 15-kg sample with a 254-mm-diameter cell, and compared results with those obtained with a 1-kg sample and a 102-mm-diameter cell.

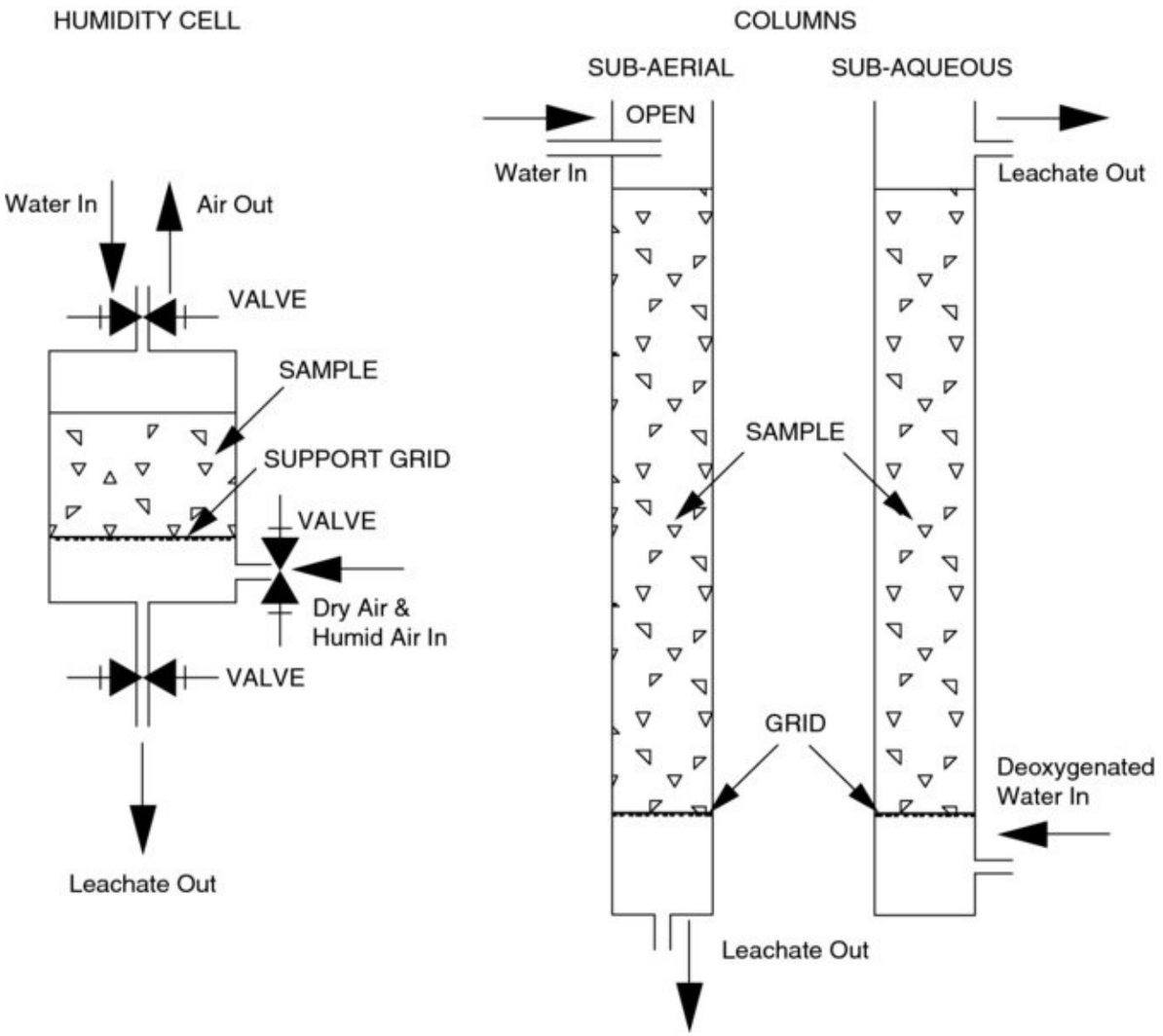

Figure 21.1 Schematic arrangements of a humidity cell and subaerial and subaqueous columns.

Other details and specifications of dry and humid air supply systems, materials of construction, and other mechanical details are provided in D5744-96. The dry and humid air systems must be capable of delivering a controlled rate of 1 to 10 L/min to each humidity cell, and flow meters are required for flow rate measurement. Columns for subaerial and subaqueous test work are typically 76, 102, or 152 mm (3, 4, or 6 in.) in diameter, and from about 1 m to more than 3 m in height. Figure 21.2 shows both subaerial and subaqueous column test work in progress.

Figure 21.2 (a) Subaerial and (b) subaqueous test work columns. (Courtesy of BC Research, Inc., Vancouver, BC, Canada.)

Humidity Cell Procedure

The humidity cell operational procedure is a cyclic one, during which the sample is subjected to 3 days of dry air permeation, 3 days of humid (water-saturated) air permeation, and 1 day of water washing (with a fixed volume of water). Caruccio (1995) has suggested that coal spoils from the eastern United States should be subjected to 6 days of humid air rather than 3 days of dry and 3 days of humid air. The procedure as described in D5744-96 is usually referred to as an *accelerated* weathering procedure because it is designed to *accelerate* the natural weathering rate of potentially acid-generating samples and reduce the length of time for which test work must be run. The artificial nature of the procedure is a consequence of regulatory constraints rather than natural ones. D5744-96 states:

1.1 This test method covers a procedure that accelerates the natural weathering rate of a solid material sample so that diagnostic weathering products can be produced, collected, and quantified. Soluble weathering products are mobilized by a fixed-volume aqueous leach that is performed, collected and analyzed weekly. When conducted in accordance with the following protocol, this laboratory test method has accelerated metal-mine waste-rock weathering rates by at least an order of magnitude greater than observed field rates.

1.6 This test method is not intended to provide leachates that are identical to the actual leachate produced from a solid material in the field or to produce leachates to be used as the sole basis of engineering design.

1.7 This method is not intended to simulate site-specific leaching conditions. It has not been demonstrated to simulate actual disposal site leaching conditions.

The procedure requires a minimum test duration of 20 weeks; however, Price (1997) recommends a minimum of 40 weeks. It is common in western Canada for humidity cells to be run for periods in excess of two years (104 weeks). It is possible that some tropical areas of the world experience climates similar to that of a humidity cell, but for North American mines the atmospheric conditions of the humidity cell are considerably harsher than the natural ones to which waste rock and tailings may be exposed. This is because:

1. Test work is usually conducted in a laboratory at room temperature, which is normally greater than the atmospheric temperature to which mining waste material is, or will be, exposed. Lower temperatures slow both chemical and biological reactions involved in acid generation. Natural site-specific water quality/chemistry (includes rain, snow, ground water) is often quite different from water quality/chemistry used in the humidity cell test work.
2. Test work ensures a rigorous dry air–moist air–water cycle to accelerate sulfide oxidation and to maximize oxidation product flushing. Most sites experience neither the regularity of the dry air/moist air cycle nor the regularity and intensity of wet precipitation corresponding to the water cycle of the humidity cell.
3. The water flush cycle of the humidity cell is conducted to ensure as completely as possible the wetting and flushing of the entire sample. Precipitation influx through waste rock dumps, and to a lesser extent tailings, is nonuniform due to channeling, and complete wetting and flushing are not achieved. Thus, the conditions of full oxygen and water supply to liberated sulfide minerals will not be achieved in practice.
4. Size reduction of waste rock or drill core, or the use of only fine fractions of waste rock, to meet the requirements of the humidity cell procedure produces sample material with a substantially greater specific surface area (m^2/kg) than that of the real waste rock and a substantially higher degree of both sulfide (acid-generating) and acid-neutralizing mineral liberation. Therefore, on a sample mass basis, a humidity cell test will potentially produce more acid (mass) and more soluble metals (mass) in a given time than will the corresponding waste rock.

A humidity cell test will usually determine *if* a given sample will “go acid” but not *when* the material from which the sample was taken will “go acid” since operation of the humidity cell has intentionally accelerated sulfide mineral oxidation. Similarly, the accelerated rate of oxidation and acid production will result in an accelerated rate of oxidation product generation as dissolved metals and/or precipitated metal compounds. That is, the metal concentrations in the weekly leachate (wash cycle) are likely to be higher than those generated in the field.

Prior to startup of a humidity cell test, the sample material must be weighed and characterized by ABA analysis, ICP multielement analysis, whole-rock major element analysis, screen sizing, and mineralogical examination. The same weighing and characterization procedure must also be conducted on the humidity cell sample residue upon completion of the humidity cell test. It is particularly important that the acid generation potential and neutralization potential of the initial and final samples be determined using identical methods. It is equally important that the initial and final samples be adequately characterized mineralogically, because some samples undergo complex mineralogical changes during the extended period of a kinetic test. Without before and after mineralogical information, it is sometimes difficult or impossible to evaluate kinetic test data.

Samples from material containing soluble sulfate minerals or previously oxidized material may require pretreatment prior to humidity cell test work to remove minerals or chemical compounds that may either mask acid generation or delay it. The preparation of humidity cell test samples should, if possible, avoid size-reduction processes (such as crushing). Tailings samples can usually be tested as is, although Price (1997) recommends the use of only the −2-mm fraction of existing waste rock dumps. Drill core must be crushed to provide samples suitable for humidity cell tests. Price (1997) recommends 80% passing 6 mm for future waste rock and ore, and 80% passing 150 µm for future tailings. The reduction of drill core to 80% passing 150 µm requires laboratory crushing and grinding, which may produce size and mineral liberation characteristics very different from those of a real mill using several stages of crushing, screening, grinding, classification, and other unit operations. It is therefore preferable that samples used for kinetic test work on future tailings be those produced from metallurgical test work.

A further particle-size-related concern in humidity cell (and column) test work is the presence of clay minerals (such as illites and smectites) of particle size less than 2 µm in the test sample. In Figure 21.1 the sample is shown supported by a grid which, in practice, is covered by a filter medium to prevent fines loss during flushing. As well as being chemically inert and nonretentive to water, this filter medium must be porous enough for the easy flow of leachate while retaining the test sample. In practice, a compromise is made with the use of polypropylene felt, or equivalent, with a filament diameter of 22 µm. Such material is unlikely to retain particles of less than 2 µm, and samples containing significant quantities of such particles will produce a leachate from flushing that will require further filtration (typically, at 0.45 µm) before dissolved metals can be determined.

A subject of considerable uncertainty at this time is whether or not humidity cells should be inoculated with bacterial cultures such as *Thiobacillus ferrooxidans* and other iron-oxidizing bacteria. D5744-96 includes instructions for the preparation of a *T. ferrooxidans* or other iron-oxidizing culture for humidity cell use and for the method of introduction of the inoculum to the rock sample. It seems likely that samples of existing waste rock, ore, or tailings would not require inoculation, whereas drill core samples might require inoculation. However, since it is generally accepted that a consortium of sulfide-oxidizing bacteria, rather than *T. ferrooxidans* alone, is required for the bacterial enhancement of sulfide oxidation rates, and since even *T. ferrooxidans* is site specific (Leduc and Ferroni, 1994), the potential benefits of an inoculum of laboratory-prepared iron-oxidizing bacteria are questionable.

The operation of humidity cells is straightforward and can be automated significantly through the use of peristaltic pumps and timers. An initial flushing of the cell is conducted by adding 750 mL (for a 1-kg sample cell) of demineralized water to the top of the cell so that the sample is thoroughly wetted. After a period of 2 h (4 h for tailings samples) the leachate is collected, weighed (for volume determination) and analyzed for pH, conductivity, acidity, alkalinity, sulfate, and dissolved metals. The measurement of leachate redox potential, Eh, may also prove useful in test interpretation. For the following 3 days, dry air is delivered to the cell at a predetermined rate, then for 3 more days humid air is delivered to the cell

(again, at a predetermined rate). The airflow rates used may be a generic standard, or they may be determined as site-specific parameters. On the seventh day the sample is flushed with 500 mL (for a 1-kg sample cell) demineralized water, allowed to stand for 2 h (4 h for tailings samples), and the leachate is collected, weighed, and analyzed for the parameters noted above. The 7-day cycle is continued until the test is terminated, whereupon the sample residue is removed from the cell, dried, weighed, and subjected to ABA analysis, ICP metals analysis, major component whole rock analysis, and mineralogical examination. Price (1997) and the American Society for Testing and Materials (1996) describe the procedure in detail.

Weekly (cycle) leachate analyses (µg/L or mg/L) are used with leachate volume (L) and sample initial mass (kg) to calculated anion and cation leaching rates (µg/kg/week or mg/kg/week). These leaching rates, along with conductivity, pH (and Eh), are plotted against cycle number (week number). The resulting curves indicate the progression of acid generation (sulfide oxidation) and neutralization. There are a variety of ways to plot the humidity cell data, including cumulative anion or cation leached and residual anion or cation not leached (initial minus cumulative leached). Normally, leachate data are plotted on a week-by-week continuous basis to monitor humidity cell progress, particularly with respect to pH. It is usual to terminate humidity cell tests after pH has stabilized at a constant value (and after the minimum number of cycles recommended by the appropriate regulatory agency). However, the presence of soluble sulfate minerals or the presence of previously oxidized material may mask or delay the onset of acid generation as noted earlier, and some samples may take 60 weeks or more to stabilize (Price, 1997). The point in time at which humidity cells are terminated is usually, therefore, site-specific, and may require considerable judgment by the project supervisor.

Table 21.1 Comparison of Sulfate Release Rates from Duplicate Humidity Cell Tests on Two Samples

	Average Sulfate Release Rates (mg/kg/week)			
Test Duration	**Sample 1**		**Sample 2**	
(20-Week Intervals)	**Cell 1**	**Cell 2**	**Cell 1**	**Cell 2**
0–20	182.5	184.1	523.3	558.7
20–40	321.8	254.6	887.1	868.1
40–60	354.8	197.5	1985.6	1481.1
60–80	306.5	192.1	1834.5	1292.1
80–100	294.0	235.0	1763.4	1247.6
100–120	227.6	141.3	3165.0	1660.7

Source: ASTM (1996).

The reproducibility of humidity cell data is not well documented. ASTM comparisons for duplicates of two samples subjected to humidity cell testing for 120 weeks are shown in Table 21.1. There is no information on either the origin of the samples or their characteristics. Data are given for the sulfate generation (release) rate. The differences between duplicates in this example are significant but may represent variability between sample splits rather than variability in cell performance. In this case it would have been particularly interesting to compare ABA analytical data and mineralogical information for the samples to determine if sulfide liberation characteristics were responsible for the differences.

Column Test Work Procedure

Column test work may be undertaken to determine the kinetic behavior of waste rock, ore, or tailings stored on the surface and exposed to atmospheric weathering (subaerial storage) or stored under water cover (subaqueous storage). In either case the aim is to monitor water (leachate) quality with time by cyclic (weekly or monthly) sampling. Unlike the humidity cell procedure, there is little, if any, standardization of column test work procedure, allowing considerable flexibility. This flexibility permits column operation to be highly site or material specific with regard to material particle size and size range (which for waste rock, ore, or drill core is usually greater than that used for humidity cell tests but still less than that of site conditions), sample mass, water infiltration or flow rate, and degree of oxygenation. Because of the lack of standardization of procedure, some regulatory agencies view column test work as supplementary to, or confirmation of, humidity cell test work rather than as an alternative to humidity cell test work. Price (1997) states that trickle leach column tests have the following disadvantages (over humidity cells):

1. The primary weathering products may be retained and therefore leachate chemistry cannot be used as a measure of the relative rates of acid generation and neutralization, and of times to mineral depletion.
2. They are run at the laboratory temperature often with a reduced particle size, and without seasonal variations and the extremes of both temperature and precipitation. Consequently, they provide poor analogues for heterogeneous drainage and the secondary mineral precipitation and dissolution, the controlling factors for metal leaching under all but the most acidic pH values.
3. Without the entire load of primary weathering products, leachate results cannot be used either with MINTEQ to predict the extent of secondary precipitation or release, or with field data to predict metal leaching based on the predicted evolution in drainage chemistry (i.e. pH conditions).

The first disadvantage listed appears to ignore the fact that humidity cell tests are intentionally *accelerated* and cannot be used to predict field rates of acid generation and neutralization; the second disadvantage is questionable, since column tests are invariably run on coarser material (except for tailings) than humidity cells and can be (and are) run with simulated site seasonal precipitation and temperature variations; and the third disadvantage appears to discount the fact that column leachate is produced from a *nonaccelerated* system in which the leachate is in equilibrium with solid oxidation products.

Subaerial column (sometimes referred to as *trickle leaching*) test work is conducted to simulate the leaching effects of precipitation infiltration to, and drainage from, material stored at the surface and exposed to the atmosphere. The water addition rate to the column may be either fixed (i.e., a certain amount per cycle) or varied to simulate the seasonal variations at the site. The column is open to the atmosphere, so there is no oxygen barrier but there is usually no forced oxygenation as with a humidity cell. Similarly, the column is operated without aggressive flushing, so that oxidation products may accumulate at particle surfaces in addition to being removed in leachate. This behavior parallels field conditions, and as a result, leachate analyses from column test work are a better indicator of expected water quality than are leachate analyses from humidity cells, particularly if the column infiltration rate is varied to simulate site conditions. Column operational temperature can also be varied to simulate site conditions, although this is rarely done.

Subaqueous column test work is conducted to simulate the leaching effects of water infiltration to and ex-filtration from material stored under water cover with no physical exposure to the atmosphere. In the case of tailings or waste rock stored under water in a natural or manufactured impoundment, infiltration of oxygenated water from the supernatant replaces any water lost by seepage to groundwater. This may be simulated in a column by the slow downward displacement of pore water by fresh water from above. In

the case of tailings or waste rock stored under water where water flow or displacement is not influenced by seepage but by thermal or density gradients (e.g., submarine storage), simulation of flow (and possible leaching) may be achieved by slow upward movement of deoxygenated water through the column (as shown in Figure 21.1), so that anoxic conditions are maintained within the rock sample and its environment. In either case the column test work conditions are adjusted to approximate as closely as possible those of the site.

Sample characterization, both before and after the test, is as important for column tests as it is for humidity cell tests. Cyclic samples are measured and analyzed (as for humidity cells) weekly or monthly, and the results are reported as µg/L or mg/L of anion or cation in leachate and µg/kg per week (or month) or mg/kg per week (or month) of anion or cation produced. Samples containing previously oxidized material or soluble sulfate minerals that may mask or delay the onset of acid generation will usually require pretreatment. The interpretation of column and other kinetic test work data is discussed on the kinetic test work interpretation page of this site.

Minewall Washing Procedure

The minewall procedure, which has seen limited use to date because it is still in the developmental phase as a procedure, requires the cyclic irrigation of a small (ca. 1 m×1 m), physically isolated area of exposed pit wall or underground rock exposure, and the collection of leachate. Physical isolation is achieved by sealing (with silicone bathroom sealant) a plastic frame (with a horizontal top, two vertical sides, and an inclined bottom for leachate capture and collection) to a rock exposure. A polyethylene sheet is used to cover the minewall assembly during leaching.

The area of exposed rock within the plastic frame is irrigated with 200 mL or more of distilled water. The runoff (leachate) is collected and analyzed. The procedure is repeated weekly and results are expressed in µg/m^2 per week or mg/m^2 per week of anion or cation (Price, 1997). The procedure is limited by the requirement that the isolated rock area be without fractures, which increase the surface area of the test by an unknown factor. Examples of humidity cell test data showing metal and sulfate leaching rates and pH are provided in Chapter 22 and shown in Figures 22.1 to 22.4.

Other Procedures

Other kinetic procedures, such as on-site lysimeters, pilot-scale kinetic test pads, and monitoring of the actual mine components, represent a major increase in scale from the procedures described above. As the scale increases, test conditions approach those of the operating (or closed) mine, so these procedures may be better described as “monitoring” than as “test work.” Most of these larger-scale options are unavailable to an ARD test work program for a new mine, where quantities of material for test work are usually severely limited.

Acknowledgments

The basic material and concepts for this chapter were developed in part by the late Chris Mills, a mining engineer specializing in metallurgical engineering and surface chemistry. He was heavily involved as an engineer in the mining industry throughout the world for over 30 years, and as a teacher and researcher he contributed many technical papers and classes on mining and acid rock drainage. Sadly, he died unexpectedly on February 10, 1999.

References

American Society for Testing and Materials (ASTM), 1996. Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell. ASTM Designation D5744-96. ASTM International, West Conshohocken, PA, 13 pp.

Caruccio, F.T., 1995. Personal communication cited in ASTM, 1996.

Lapakko, K.A., 2003. Developments in Humidity-Cell Tests and Their Application. In: J.L. Jambor, D.W. Blowes and A.I.M. Ritchie (eds.), Environmental Aspects of Mine Wastes, Short Course Series, Mineralogical Association of Canada, Québec, Canada, vol. 31, pp.147--164.

Lawrence, R.W., 1995. Prediction of acid rock drainage: fundamentals and tools. Notes from a MEND Workshop, Montreal, PQ, Canada, December 7–8, 27 pp.

Leduc, L.G., and Ferroni, G.D., 1994. The Need for *Thiobacillus ferrooxidans* Strain Selection in Applications of Bioleaching. In: Proceedings of Biominet, 10th Annual General Meeting, Minister of Supply and Services, Ottawa, ON, Canada, pp. 25–42.

MEND, 1995. MINEWALL 2.0. Series of four reports: Literature Review, User's Guide, Application of MINEWALL to Three Minesites, and Programmer's Notes and Source Code, plus one diskette. MEND, Ottawa, ON, Canada.

Perkins, E.H., Nesbitt, H.W., Gunter, W.D., St.-Arnaud, L.C., and Mycroft, J.R., 1995. Critical Review of Geochemical Processes and Geochemical Models Adaptable for Prediction of Acidic Drainage from Waste Rock. MEND Report 1.42.1. MEND, Ottawa, ON, Canada, 120 pp.

Price, W.A., 1997. Draft Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia. British Columbia Ministry of Employment and Investment, Energy and Minerals Division, Smithers, BC, Canada, 143 pp.

Soregaroli, B.A., and Lawrence, R.W., 1998. Update on waste characterization studies. Presented at the Mine Design, Operations and Closure Conference, Polson, MT, 10 pp.

U.S. Environmental Protection Agency, 2001. Method 1627: Kinetic Test Method for the Prediction of Mine Drainage Quality. EPA-821-R-09-002. U.S. EPA, Office of Water, and Office of Science and Technology, Engineering and Analysis Division (4303T), Washington, DC, 33 pp.

22
Kinetic Testing Data Interpretation

BRUCE W. DOWNING

The interpretation of kinetic test work results varies from straightforward to extremely difficult, depending on the mineralogy of the samples tested, their origin, and their history. For all but the simplest cases, valid interpretation depends on solid knowledge of sample petrology and mineralogy, size distribution and liberation characteristics, acid–base accounting data, and geological, hydrological, meteorological, and other relevant data. An extensive review of kinetic geochemical processes and their relevance to the assessment of waste rock acid rock drainage (ARD) potential is documented by Perkins et al. (1995). Case studies regarding data interpretation are reviewed by Morin and Hutt (1997).

Introduction

When kinetic tests are conducted on previously oxidized material such as waste rock or ore stockpiles, or tailings, it must be assumed that particle surfaces, including cracks and fissures, may contain water-soluble oxidation products such as sulfates and/or hydroxy sulfates. These compounds will dissolve as the kinetic test proceeds and will be recorded as cations and (usually) sulfate ions generated by the sample. While the cations and sulfate are the products of ARD, they are not the products of sulfide oxidation during the kinetic test itself, since they may have accumulated over a period of many years. Also, since most of these products accumulate at the particle or grain boundaries of sulfide minerals, they will, to varying degrees, tend to protect the sulfide mineral grains from further oxidation. For work conducted at the Island copper mine in British Columbia, Dagenais and Poling (1997) stated that "… kinetic testing conducted on previously oxidized material spent many weeks of expensive test work leaching reaction products from the material before rates of sulfide oxidation could be calculated."

Kinetic tests on previously oxidized material will usually generate results that potentially show both the dissolution and the generation of oxidation products. Depending on reaction kinetics, these two separate phenomena may generate either overlapping or separate cation–anion production rate–time curves. It is possible, therefore, that dissolution rates from oxidation products may mask generation rates from sulfide oxidation.

The following two examples are from data obtained from column test work on waste rock dumps at the United Keno Hill mines in the Yukon Territory as reported by Access Mining Consultants Ltd. (1996). Figure 22.1 shows sulfate, calcium, magnesium, and zinc leaching rates and pH for a waste dump quartzite sample containing 0.14% sulfide-sulfur and less than 0.01% sulfate-sulfur with AP = 4.4 kg/metric ton (mt) $CaCO_3$, NP = 3.2 kg/mt $CaCO_3$, NNP = −1.2 kg/mt $CaCO_3$, and NPR = 0.7. This is a sample that would be expected to be acid generating.

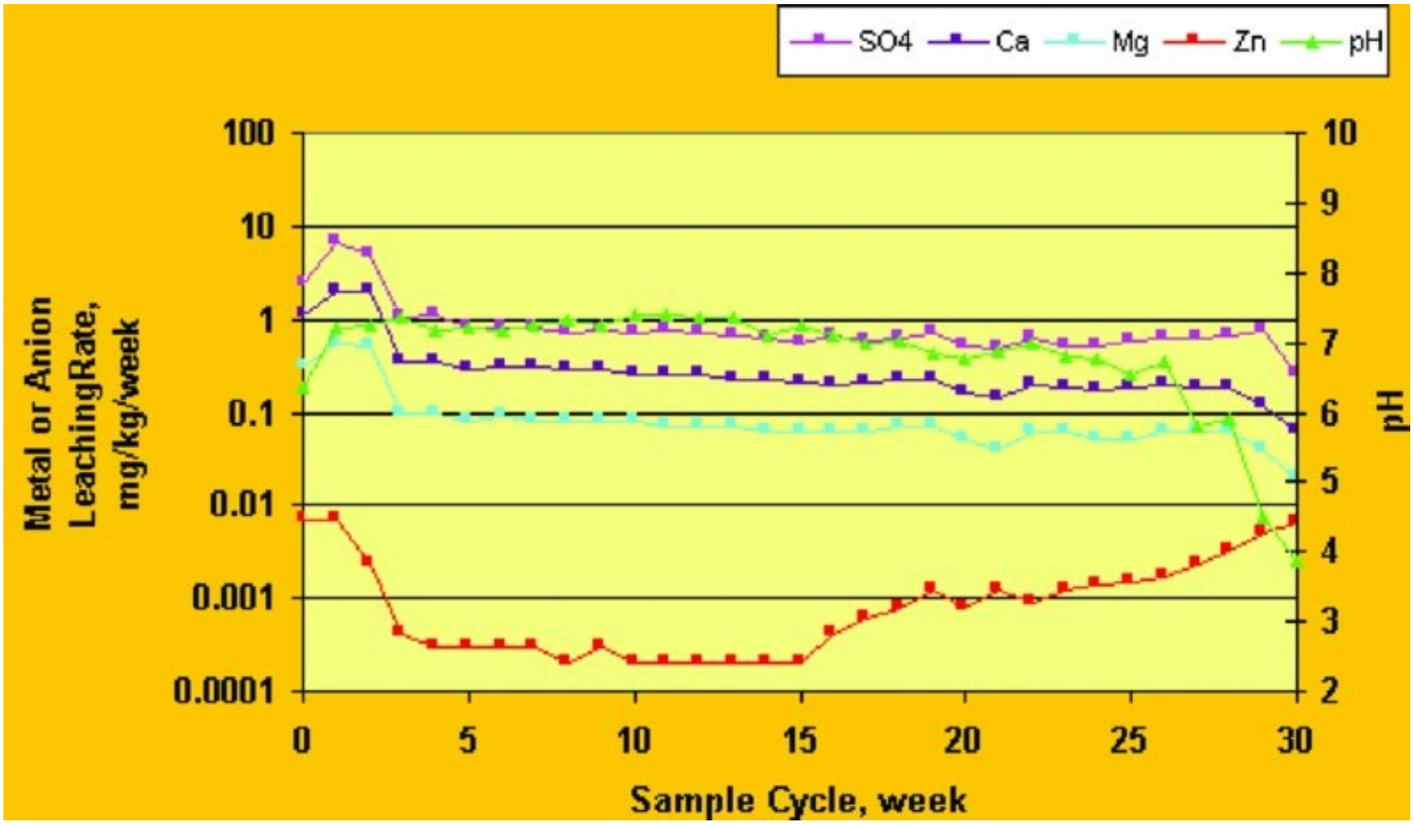

Figure 22.1 Metal and sulfate leaching rates and pH for subaerial column testing on Keno Hill waste dump quartzite. (Data from Access Mining Consultants Ltd., 1996.)

The sample clearly is acid generating, but only after a period of about 14 weeks. During these initial 14 weeks, sulfate generation, paralleled by calcium and magnesium generation, is probably from accumulated gypsum. It might be argued that the calcium and magnesium could equally well be produced from acid generation and neutralization until, after 14 weeks, acid generation exceeded neutralization capability. Nevertheless, calcium and magnesium generation clearly continue at a pH-independent rate from week 14 to week 28. In addition, zinc generation initially falls, independently of pH, suggesting the dissolution of residue, and then rises with pH, suggesting primary mineral reaction. It is likely that the curves of Figure 22.1 represent a case of overlapping residue dissolution and acid generation as the source of dissolved ions.

Figure 22.2 shows sulfate, calcium, magnesium, copper, iron, and zinc leaching rates and pH for a mixed-vein quartize and schist waste dump sample containing 0.38% sulfide-sulfur with AP = 11.9 kg/mt $CaCO_3$, NP = 0 kg/mt $CaCO_3$, NNP = −11.9 kg/mt $CaCO_3$, and NPR ≤ 0.1. The sample was from a waste dump more than 20 years old in which acid generation and neutralization had clearly taken place to the exhaustion of available neutralization capability. Based on ABA data alone this is a sample that would be expected to be acid generating from oxidation of the remaining sulfide-sulfur.

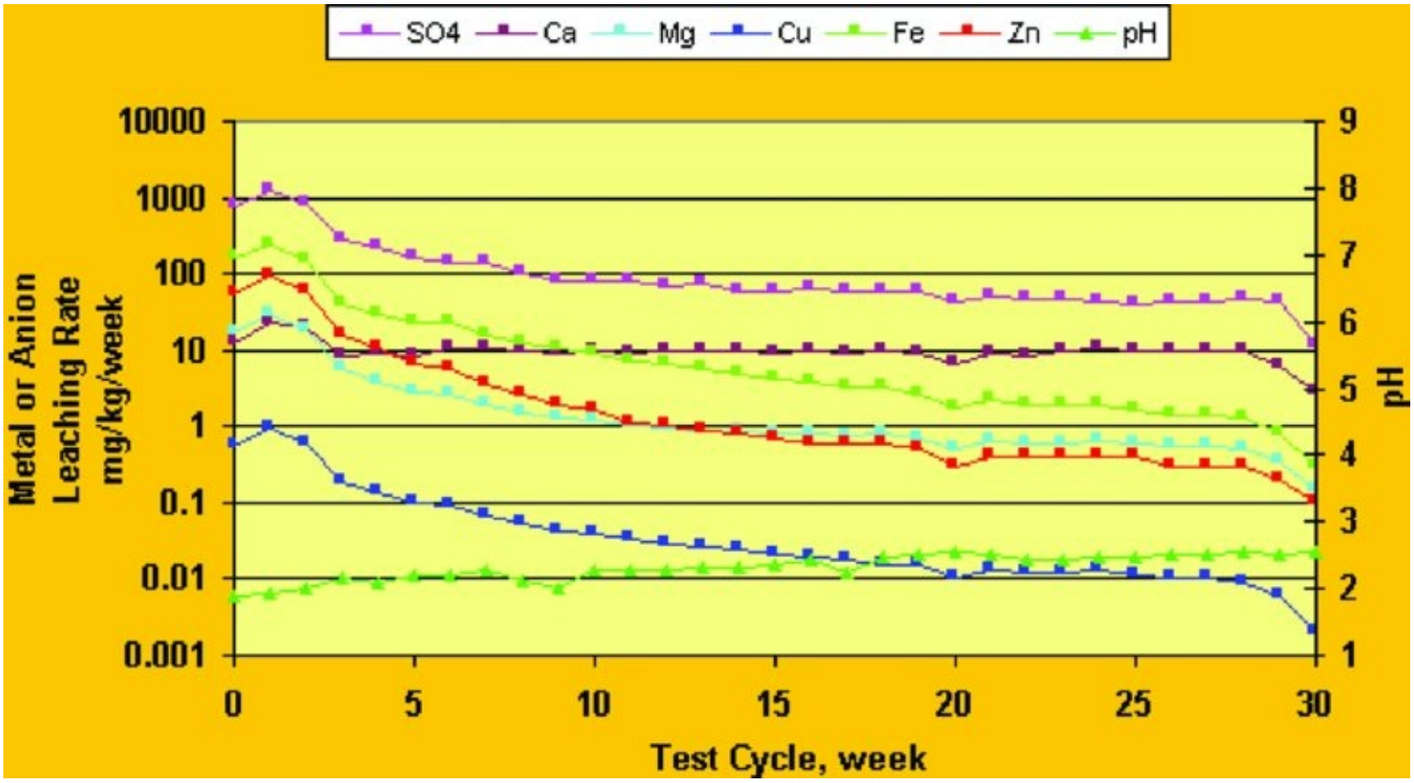

Figure 22.2 Metal and sulfate leaching rates and pH for a subaerial column test on Keno Hill waste dump mixed-vein quartzite and schist. (Data from Access Mining Consultants Ltd., 1996.)

All of the metal and sulfate leaching rates are initially high and fall steadily by one to two orders of magnitude over 27 weeks, showing some stability between weeks 12 and 27 (sulfate, calcium, and magnesium) and weeks 20 and 27 (iron, copper, and zinc). There appears to be a significant fall in leaching rates for all metals and sulfate after week 27. pH increases slowly, but steadily, from pH 1.9 to pH 2.5 at week 30. The low pH values are the result of metal ion hydrolysis (see, e.g., Hughes and Maloney, 1964) in the sulfate environment, not from sulfide oxidation, and the pH increase with time reflects the decrease in metal ion concentration with time. The pH values agree well with predictions generated by the computer geochemical equilibrium speciation model MINTEQA2 (Allison et al., 1991) using leachate cation and anion aqueous concentrations.

Overall, the curves of Figure 22.2 are indicative of the dissolution of accumulated oxidation products. These products *might* include gypsum ($CaSO_4$), melanterite ($FeSO_4 \cdot 7H_2O$), copiapite [$Fe_5(SO_4)_6(OH)_2 \cdot 20H_2O$], roemerite [$Fe_3(SO_4)_4 \cdot 14H_2O$], kornelite [$Fe_2(SO_4)_3 \cdot 7H_2O$], coquimbite [$Fe_2(SO_4)_3 \cdot 9H_2O$], rhomboclase [$HFe(SO_4)_2 \cdot 4H_2O$], halotrichite [$FeAl_2(SO_4)_4 \cdot 22H_2O$], mallardite [$MnSO_4 \cdot 7H_2O$], brochantite [$Cu_4(SO_4)(OH)_6$], chalcanthite [$CuSO_4 \cdot 5H_2O$], boothite ($CuSO_4 \cdot 7H_2O$), zinc-melanterite [$(Zn,Cu,Fe)SO_4 \cdot 7H_2O$], smithsonite ($ZnCO_3$), and hydrated oxides of iron such as ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) and goethite [FeO(OH)].

Since the sample has no NP, there can be no formation of gypsum by acid neutralization and soluble calcium, and corresponding sulfate must derive from existing gypsum dissolution. However, gypsum alone would not account for the very high initial sulfate generation rate, and the difference in shape of the sulfate and calcium curves through approximately week 14 tends to confirm this. Some other soluble sulfate minerals containing iron, manganese, copper, and zinc are noted above.

The continuous shape of the sulfate curve is not indicative of acid generation by sulfide oxidation. It

would be expected that oxidation of the 0.38% sulfide-sulfur in the sample would begin only after oxidation products at sulfide grain surfaces were sufficiently depleted to allow oxygen and water diffusion to the sulfide grains, as can be seen in the later weeks in Figure 22.1. For Figure 22.2**,** it is clear that after 30 weeks there is still dissolution of oxidation products.

To bypass the stage of oxidation product dissolution in kinetic testing of potentially acid-generating, previously oxidized material (and to thus reduce the length of time for kinetic testing), Dagenais and Poling (1997) examined the effects of sample pretreatment with distilled water and sulfuric acid–acidulated water of pH 4 and 2. They concluded that (for the Island copper waste rock), pretreatment with sulfuric acid at pH 2 removed 70% of the accumulated oxidation products from their samples. Price and Kwong (1997) refer to a procedure for oxidation product removal using a dithionite–citrate solution buffered with sodium bicarbonate.

Material Containing Soluble Sulfate Minerals

Materials containing soluble sulfate minerals such as gypsum and anhydrite require special consideration in kinetic test work. Mineralogical test work and an ABA program in which both sulfate-sulfur and sulfide-sulfur are determined will clearly identify the presence and mode of occurrence of these minerals. Unlike sulfates and hydroxysulfates in previously oxidized material, natural occurrences of gypsum and anhydrite do not occur specifically on sulfide mineral surfaces, but as discrete grains and aggregates, often in cracks and veinlets. However, from startup of the kinetic test the minerals will dissolve to give calcium and sulfate ions in solution, and the concentration of these ions is likely to be large enough to completely mask the concentration of any calcium or sulfate produced by sulfide mineral oxidation or neutralization. In addition, since sulfate ion is a product of both sulfide mineral oxidation and gypsum or anhydrite dissolution, the concentration of sulfate ion from mineral dissolution may be high enough to suppress sulfide oxidation to sulfate because of the common-ion effect. It may take many weeks or months for all of the gypsum or anhydrite to dissolve, and during this period the onset of sulfide oxidation and acid production will almost certainly be delayed, even for samples that are clearly potentially acid generating based on ABA test work.

The following two examples are from test work on materials (crushed drill core) from the Huckleberry mine in British Columbia. These data are not in the public domain but were generously supplied by Peter Campbell, the manager of environmental affairs at Huckleberry Mines Ltd. The test work was performed by Richard Lawrence, University of British Columbia. The mineralogy of the Huckleberry deposit in relation to ARD has been discussed by Mills (1995).

Figure 22.3 shows humidity cell results for a sample of low-grade ore over a period of 125 weeks. This ore contained 4.15% total sulfur and 2.98% sulfide-sulfur. The difference, sulfate-sulfur, accounted for 1.17%, which was contributed by gypsum and anhydrite. ABA data for the sample: AP = 93 kg/mt $CaCO_3$, NP = 72 kg/mt $CaCO_3$ (modified Sobek), and NPR = 0.77. This sample would be expected to be acid generating.

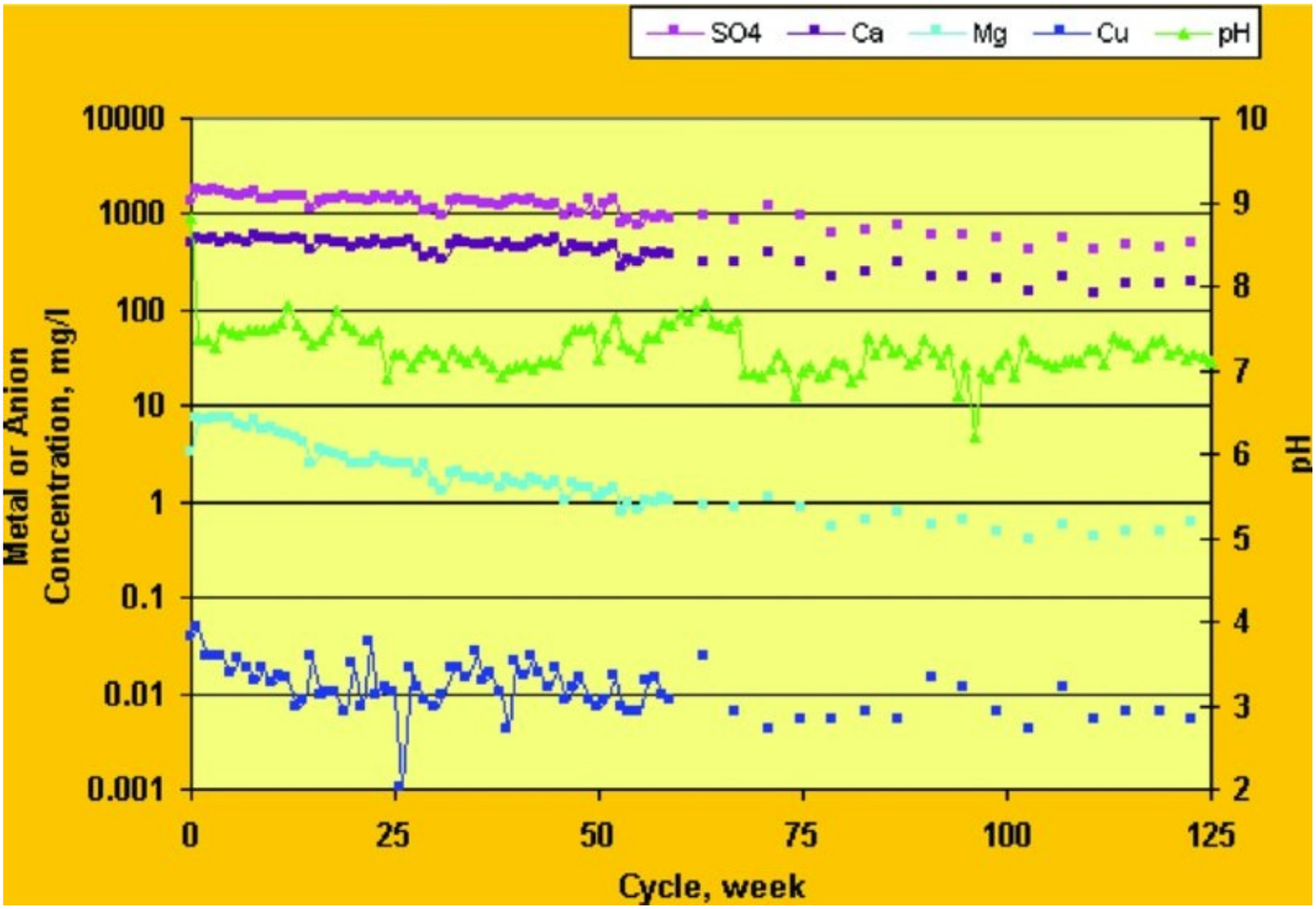

Figure 22.3 Metal and sulfate leaching concentrations and pH for a humidity cell test on Huckleberry mine low-grade ore. (Data courtesy of Peter Campbell, Huckleberry Mines Ltd.)

Despite the potential for acid generation, Figure 22.3 clearly shows that the cell leachate remained at or about pH 7 for the 125 weeks of the test. Calcium and sulfate leaching rates fell slightly over the test period while maintaining an almost constant ratio, corresponding to the calcium/sulfate ratio of gypsum or anhydrite. The figure is therefore a demonstration of gypsum and anhydrite dissolution from the low-grade ore. If any acid generation or neutralization took place, it is masked by sulfate mineral dissolution. The relatively constant and low level of copper leaching (Huckleberry is a copper ore) is consistent with the dissolution of gypsum and anhydrite rather than acid generation or neutralization. The humidity cell test work period of 125 weeks is much longer than is normally used, but even after this period, a clearly potentially acid-generating sample was still neutral and dominated by gypsum and anhydrite dissolution.

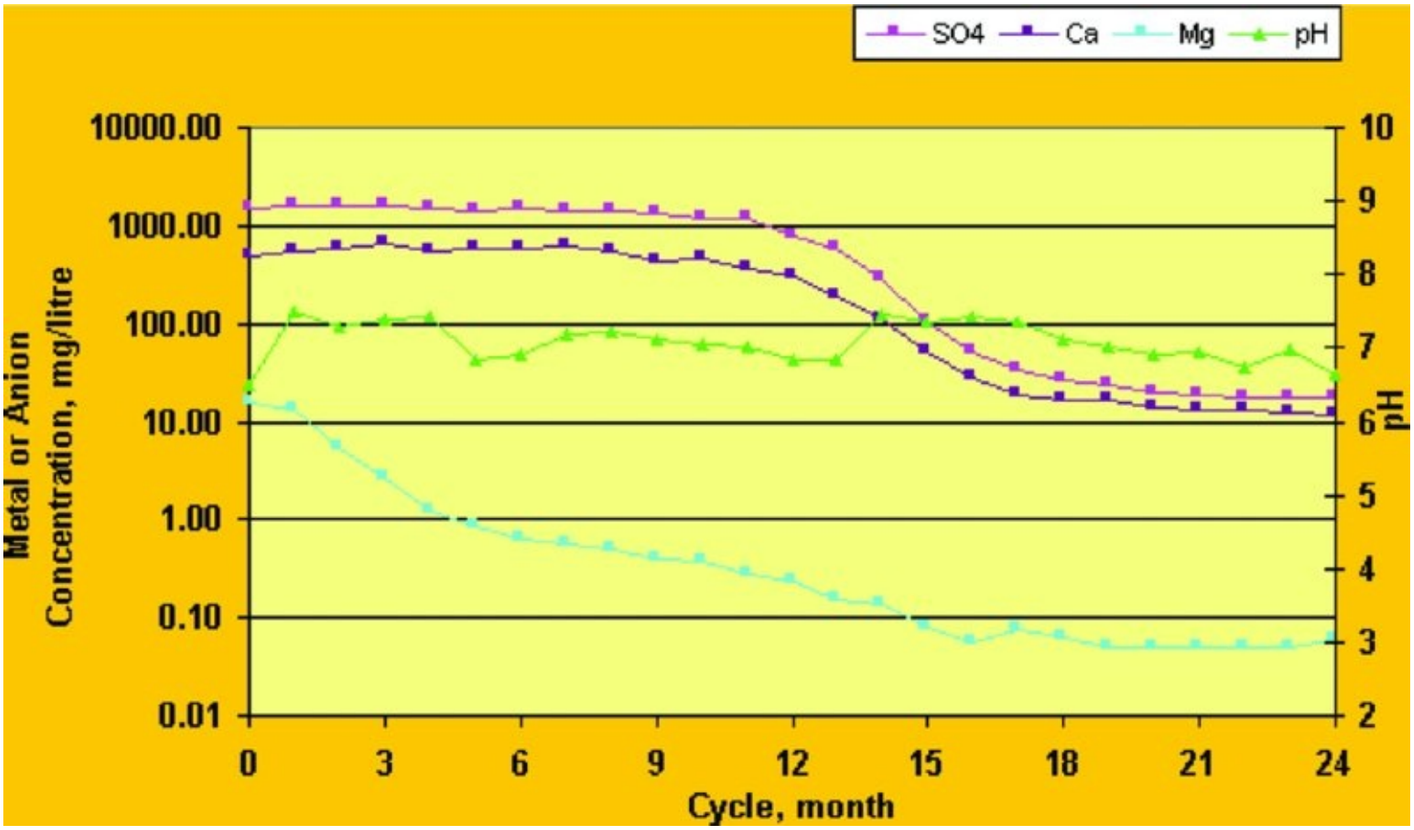

Figure 22.4 Metal and sulfate leaching concentrations and pH for a subaqueous column cell test on Huckleberry mine volcanic waste rock. (Data courtesy of Peter Campbell, Huckleberry Mines Ltd.)

Figure 22.4 shows the results of 24 months of column test work to evaluate the subaqueous disposal of potentially acid-generating volcanic waste rock with NPR = 0.2. In addition to sulfides, this sample contained significant gypsum and anhydrite. Figure 22.4 differs markedly from Figure 22.3, in that it shows a significant decrease in calcium and sulfate leaching rates beginning at about month 11 and leveling off at about month 17. Between months 11 and 17, these leaching rates fell by two orders of magnitude, and this is interpreted as coinciding with the practical depletion of liberated gypsum and anhydrite in the sample. With an NPR of 0.2, this sample would be expected to oxidize and generate acid after gypsum and anhydrite depletion. However, this test was conducted to simulate subaqueous deposition with water as the oxygen barrier, and the absence of oxidation and acid generation is demonstrated by the relatively constant pH 7 of the system throughout the entire 24 months of the test.

Acknowledgments

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References and Suggested Reading

Access Mining Consultants Ltd., 1996. United Keno Hill Mines Limited: Geochemical Testing Report—Progress Report 1. AMC, Whitehouse, YT, Canada.

Allison, J.D., Brown, D.S., and Novo-Grada, K.J., 1991. MINTEQA2/PRODEFA2: A Geochemical Assessment Model for Environmental Systems, Version 3.11. EPA/600/3-91/021. U.S EPA, Office of Research and Development, Athens, GA.

American Society for Testing and Materials, 1996. Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell. ASTM Designation D5744-96. ASTM International, West Conshohocken, PA, 13 pp.

Dagenais, P.J., and Poling, G.W., 1997. An investigation into the geochemical history of a waste rock dump and its effect on water quality of the flooded open pit at island copper mine, Port Hardy, British Columbia. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 1709–1726.

Hughes, D.E.P., and Maloney, M.J., 1964. Advanced Theoretical Chemistry. Chatto & Windus, London, pp. 139–140.

Mills, C., 1995. Technical Review of the Acid Rock Drainage (ARD) and Metal Leaching Aspects of the Metallurgical Test Work, Milling Practices and Tailings Monitoring for the Huckleberry Project. Report (draft) to BC Ministry of Energy, Mines and Petroleum Resources, Vancouver, BC, Canada, 34 pp.

Morin, K.A., and Hutt, N.M., 1997. Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies. MDAG Publishing, Vancouver, BC, Canada, pp.

Perkins, E.H., Nesbitt, H.W., Gunter, W.D., St.-Arnaud, L.C., and Mycroft, J.R., 1995. Critical Review of Geochemical Processes and Geochemical Models Adaptable for Prediction of Acidic Drainage from Waste Rock. MEND Report 1.42.1. MEND, Ottawa, ON, Canada, 120 pp.

Price, W.A., and Kwong, Y.T.J., 1997. Waste rock weathering, sampling and analysis: observations from the British Columbia Ministry of Employment and Investment database. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 31–45.

Rescan Environmental Services Ltd., 1997. Tulsequah Chief Project Report, Vol. IV. Rescan, Vancouver, BC, Canada.

Soregaroli, B.A., and Lawrence, R.W., 1998. Update on waste characterization studies. Presented at the Mine Design, Operations and Closure Conference, Polson, MT, 10 pp.

23
Block Modeling and Acid Rock Drainage Prediction

BRUCE W. DOWNING AND GARY GIROUX

Waste rock and material modeling and characterization with respect to acid rock drainage (ARD) variables should be an integral part of a resource estimation study. In this chapter we discuss the potential sources of ARD in an open-pit mining context and the characterization of waste rock variables by block modeling and geostatistical estimation for ARD prediction purposes. A case history is presented. Waste rock limits will ultimately depend on the economics of minable commodities, but caution should be noted where waste rock may be uneconomical at present commodity prices but economical at higher commodity prices and thus not necessarily included in the ARD waste material.

Introduction

Many deposits provide challenges in resource estimation, including not only the quantity of minable minerals in a deposit but also the amount and location of materials that might have implications for environmental impact during development, operation, closure, and postclosure/remedia-tion. The potential for ARD from waste material is recognized as a key issue in project planning in the following areas:

- Mine planning and scheduling in the pit and in waste dump(s)
- Waste material dump handling and treatment, whether surface or under water
- Pit wall and pit floor hydrology and ARD modeling
- Tailings storage
- Proper design of kinetic and humidity cell test work
- Proper sampling for waste material characterization
- Reclamation and closure planning, which depend essentially on waste material removal
- Use of waste material for construction
- Waste material blending
- Salvage of topsoil
- Design of waste rock dump (and water treatment facility, if needed)

A waste material estimate must be calculated in conjunction with the resource estimate because of the importance of mine waste disposal (Figure 23.1). ARD waste material includes overburden, waste rock, pit walls, pit floor, and tailings, which for regulatory and permitting purposes should be classified as acid generating, potentially acid generating, potentially acid consuming, or potentially neutral. The initial ARD study should begin at the exploratory stage, when management deems the deposit to have the potential to be an economically feasible operation (Claridge and Downing, 1992).

The type of predictive ARD block model that is used should be decided by a qualified person. It will be used in long-range planning and production decisions which lead ultimately to estimation of the disposal

costs associated with a block of waste rock. This is very important, since each waste block must be treated separately as to its mode of removal or salvage, placement, and subsequent treatment.

It is not our purview in this chapter to present a dissertation on geostatistical computations involved in block modeling but to use the method to show that the amount of waste material should be determined in conjunction with the resource calculation and to present some ideas on methodology. Waste rock modeling has been included in at least two studies reported in the literature: Downing and Giroux (1993) and Bennett et al. (1997). We have found from other resource studies that waste rock block modeling is generally not part of any resource estimation, at either the prefeasibility or feasibility stages.

There are two main components of the block model:

1. Estimate the acid generation potential of waste material.
2. Estimate the metal or trace element component of the waste material that would affect the metal-leaching (ML) component of an ML/ARD program.

Waste Material

Waste material is deemed to be any material that does not have a positive economic value at the time of feasibility other than a disposal and treatment or remediation value. Potential waste material includes topsoil, overburden, waste rock, and tailings. It should be noted that waste rock determination may change with increasing or decreasing commodity prices.

Overburden

Overburden is a term used by geologists and engineers to designate material of any nature, consolidated or unconsolidated, that overlies a deposit of useful materials, ores, or coal, especially those deposits that are mined from the surface by open cuts. For others, *overburden* designates only loose soil, sand, gravel, and so on, that lies above the bedrock (e.g., Thrush et al., 1968). In northern climates, permafrost may be considered a special type of overburden; in southern climates, saprolite may be considered overburden. Overburden for the reclamation stage would designate the organic horizon(s) as a special overburden category, as it is collectively removed as a soil salvage operation and stockpiled and treated separately for reclamation purposes.

The ARD assessment of overburden is necessary because it may be used for borrow material for roads, land fill, and dams. The overburden affects groundwater in terms of chemistry and flow. It also has a direct impact on surface water quality in terms of water runoff and erosion contributing to sedimentation in streams. There will be an impact on groundwater quality if mineralized materials are incorporated into the overburden, depending on their particle size, quantity, and distribution.

Waste Rock

The ARD evaluation of waste rock is necessary to assess any potential acid-generating waste rock that will have to be monitored and stockpiled. Some of the non-acid-generating rock may be used for construction material for roads, land fill, and so on. It should also be noted that glacial ice may be considered as waste rock (Downing and Giroux, 1993), with the advantage that it disappears with time. Waste rock will have been determined based on grade cutoff value(s). The lithogeochemical difference between the hanging wall and footwall waste rock lithologies must be investigated and a distinction made

when estimating the impact on the waste rock ARD block model.

Pit Wall and Pit Floor

ARD assessment of the pit walls and floor is necessary, as they will have an impact on water quality during mining operations and postmining, until the pit eventually fills with water. The upper exposed walls will not be covered and have the potential to generate ARD if they contain any acid-generating material. Closure and postclosure remediation plans generally include modeling the pit filling and pit lake chemistry (Bursey et al., 1997).

Tailings

ARD assessment of tailings is necessary because they will have an impact on the method of tailings disposal, whether it be surface, subaqueous, or submarine impoundment. The reserve estimate in conjunction with the mineral process flow sheet will give an estimate of the amount of tailings that will be generated by mining. This is critical in designing the proper tailings storage facility.

Sampling

Sampling procedures for the deposit consist of surface and underground drilling, surface and underground chip sampling, underground and surface bulk sampling for metallurgical testing, and minor amounts of trenching. It is imperative that the deposit be sampled properly so that reliable estimates can be made according to the industry standard definitions of reserve and resource. There is no finite number of samples for ARD studies, but the question should be: Will the number of samples be sufficient to construct a waste rock block model that will characterize each waste block with some confidence? This may necessitate carrying out waste rock drilling in order to have sufficient sampling to properly characterize the outlying waste blocks and provide some confidence in extrapolating to other less sampled areas using an appropriate interpolation method. Additional holes will generally have to be drilled to define waste rock boundaries and for sampling to produce data for block modeling. Figure 23.1 shows the loading process at a shallow strip mine.

Figure 23.1 Loading process at a typical shallow strip mine in western North America.

Core logging is vital to the block model process. Lithological, mineralogical, structural, and geotechnical data are entered into the site computer database. The geotechnical data have important ramifications for pit wall modeling. Specific gravity should be measured on-site using core samples regardless of rock type, so as to calculate material mass. There will be some variation in specific gravity measurements, due to variable lithology, mineralogy, and inclusions. Particular variants include amounts of sulfides and magnetite in waste rock. It is imperative that an accurate and detailed geological and assay geochemical database be established for resource studies and that geological drill logs be designed to incorporate greater detail in conjunction with sampling for ARD. Quality assurance/quality control (QA/QC) and data verification should be carried out in accordance with good management practices.

Block Model

To produce a meaningful block model containing estimates of ARD values, a database of ARD parameters, similar to a resource estimate database, is required. Analytical data include neutralization potential (NP) as determined from acid–base accounting analyses (ABA), sulfide-sulfur analyses (assuming that the sulfur is attributable to sulfides rather than sulfates) and inductively coupled plasma mass spectroscopic (ICP-MS) analyses. The calcium and magnesium values from ICP-MS analyses are useful in determining the potential neutralizing potential, although caution must be noted as to whether calcium and magnesium are attributable to carbonates rather than silicates, as over time the former contributes neutralization at a faster rate than the latter. Visual and mineralogical observations together with analytical data can provide an effective means of predicting which waste rock types will be acid

generating (AG), potentially acid generating (PAG), potentially acid consuming (PAC), and/or potentially neutralizing (PN). From ABA studies and geological data together with laboratory (humidity cell) and field weathering tests, it should be possible to predict acid generation characteristics of waste rock throughout the deposit. A major problem with any waste rock block modeling is the lack of availability of data points in waste rock, as most drilling is involved with delineating ore. Drilling specifically to delineate waste rock is generally not an accepted method at the feasibility stage; however, it provides vital data that are needed for a comprehensive waste material management plan. During most drilling programs, the waste rock is never sampled and thus data points for block modeling are not available. Generally, if the entire drill hole is assayed, sufficient meaningful data points may be available for modeling. Blast hole sampling for grade control can also be used for ARD purposes, as cuttings are generally sent to the mine laboratory, and subsequently, a subsample can readily be analyzed for sulfur and neutralization potential.

Major elements have been investigated as to their potential use as an inexpensive surrogate method in lieu of the neutralization potential (NP) (Downing and Madeisky, 1997, 1999). One of the first studies was the use of % Ca versus NP plots in the estimation of PAC material for the waste block ARD model from the Windy Craggy massive copper sulfide deposit (Downing and Giroux, 1993). The NP was attributable to carbonate mineralization; hence, leachable Ca was analyzed using a 30-element ICP-MS method following an aqua regia digestion. Day (1995) used Ca + Mg concentrations determined by ICP (following an aqua regia digestion) as a surrogate for NP. An ARD orientation study using Ca and Mg analyzed using the ICP-MS method would provide the necessary information as to whether the NP is attributable to carbonates. If a correlation does exist, all samples should be analyzed using the ICP method since this would also provide some QA/QC to NP determinations. The ICP analysis is much cheaper than NP determinations, thereby allowing many more samples to be characterized as AG, PAG, PAC, and/or PN. Generally, an ICP instrument is not found in most mine laboratories; however, Ca and Mg can also be measured adequately using an atomic absorption emission spectrometer, which many mines have on site. If a correlation can be made between CO_2 and Ca, and assuming that CO_2 is indicative of carbonate and that no graphite is present, a Leco carbon analyzer can be used. With the advent of portable spectrometers, rapid on-site determinations can be made for Ca, Mg, and sulfur. An orientation survey needs to be conducted to show the regulatory people that these methods have merit and are applicable to the mine-site ARD test work program.

A block model is a three-dimensional spatial representation to quantify the geology and economics of a deposit, which in turn is used in mine planning (see Figures 23.2 and 23.3). Blocks may be of uniform size (i.e., 10 × 10 × 10 m) or they may be of variable dimensions that depend on the mining plan. The limits for the block model should be chosen to include the proposed pit outlines plus additional areas for pit enlargement(s) and to cover possible mineralization beyond the known deposit limits. The actual waste blocks that would be removed are dependent on the mining plan. As more closely spaced data become available, the model can be refined.

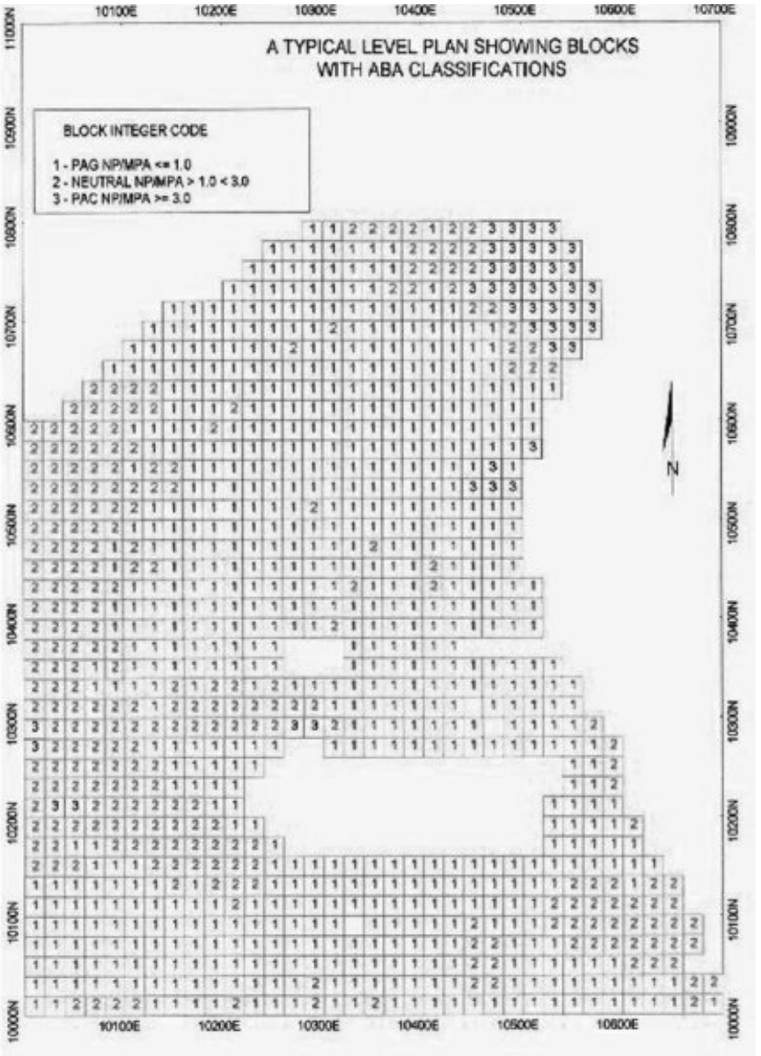


Figure 23.2 Plan view showing rock units with ABA classifications. Red: PAG, NP/MPA ≤ 1.0; green: neutral, NP/MPA > 1.0 < 3.0; blue: PAC, NP/MPA > 3.0.

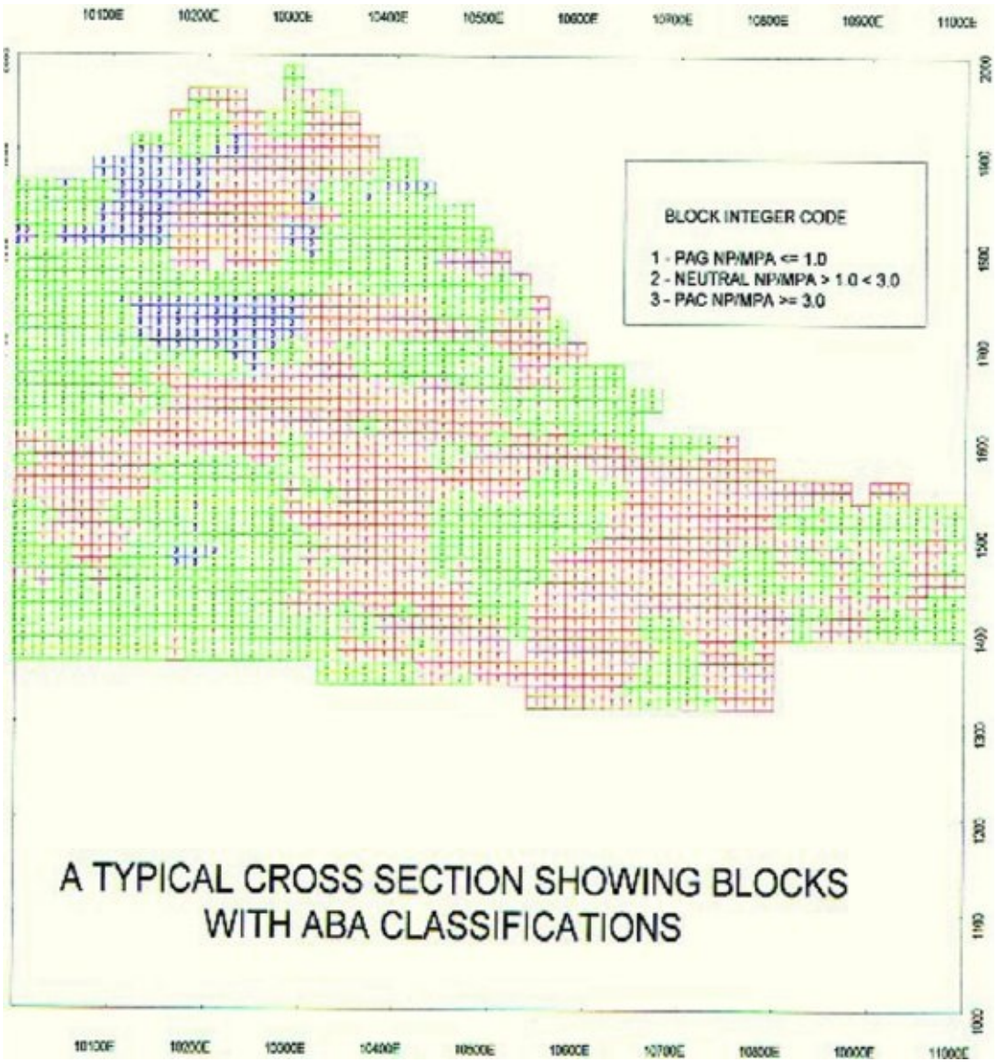


Figure 23.3 Typical cross section showing rocks units with ABA classifications. Red: PAG, NP/MPA ≤ 1.0; green: neutral, NP/MPA > 1.0 < 3.0; blue: PAC, NP/MPA > 3.0.

The first step in building a block model for any variable is to produce a detailed geological interpretation that can be converted into a three-dimensional geological solid model. The solids should be built by those geologists most familiar with the project, as this step often entails subjective decisions of boundaries and contacts of individual geological units. The procedure is usually accomplished by interpreting geological contacts from drill hole core logging on cross sections cut through the deposit. The interpreted contacts are digitized, using any one of numerous software packages available. The interpreted contacts, limits of geological domains, and drill hole traces are then plotted on level plans cut at reasonable intervals, often the proposed mining bench height, from the topographical surface down to the lower limits of mining. The contacts and domain limits are drawn on each level plan joining the interpretations from each cross section. This is often a difficult process that requires a high level of subjectivity, hence the reason for involving the geologists most familiar with the project. This stage of geological modeling is normally completed for any resource or reserve estimation and may not require much, if any, change to use in an ARD study.

The next step consists of reclassifying drill hole data, in terms of the geological model being interpreted. Often, small intersections, of a particular rock unit, will be incorporated within larger solids of a different rock unit, during the modeling stage. Thus, downhole geological drill logs should not be used to determine limits of grade composites. Instead, drill hole data should be compared with the three-

dimensional solids, and the entry and exit points of each drill hole through each solid should be recorded. The subsequent data file containing hole number, from, to, and geological unit code can be used to form uniform downhole composites that truly honor geological boundaries. For an unbiased estimate, all data should be composited to a uniform support (i.e., composite length ± one-half the composite length). At the boundaries of each geological unit, small composites, less than one-half the composite length, may have been formed. These small intersections should be recombined with the adjoining sample, to avoid the loss of any assay data.

Once composites for the variables to be estimated have been produced, they should be evaluated as a function of rock code. Simple statistics, consisting of mean, standard deviation, and coefficient of variation and histograms, should be produced for each variable, and compared. Geological domains exhibiting similar distributions can be combined.

Given sufficient data to model, variography can be used to predict anisotropy and ranges of continuity for each variable. Semivariograms should be produced for each variable within each geological domain. Semivariograms allow for consideration of a sample's position in space, in addition to its distance from the block during the weighting of samples in interpolation. A knowledge of the range of continuity and anisotropy, if present, also aids in designing infill drill patterns.

The final stage of producing a block model for ARD characteristics consists of interpolating a value into each block for each variable. The geological code for each block, from the block model, determines which composites and which model will be used for the estimate. For example, in the Windy Craggy case history (Downing and Giroux, 1993), calcium was kriged for each block in the model using ICP values, present in most assayed samples, while sulfur was estimated by the inverse-distance-squared method. An example of using surrogate analyses is presented in Figure 23.1. In this case, sulfur was available only in ARD samples and those taken for specific gravity (2999 samples with sulfur analyzed compared to 21,416 sampled with calcium values). As a result, semivariograms for sulfur could not be produced for all the geological domains. Figure 23.2 shows an example of the distribution of the various lithologies at Windy Craggy.

The criteria for characterizing waste rock as AG, PAG, PAC, and PN are site dependent and may be arrived at from static and kinetic test work and regulatory permitting. If several block models have been tried, the criteria for classifying waste blocks might be two out of three ratios to meet the acceptable PAG, PAC, or PN value. Each block may have various components composed of PAG, PAC, and PN material. Figure 23.3 shows an example of the distribution of ABA classifications at Windy Craggy, which can be compared with Figure 23.2.

Data that are needed for modeling waste rock must include total sulfur, CO_2 (short-term buffering effect), Ca, Mg, and NP. Once the model and subsequent ABA database have been constructed, they should be updated continually from the (daily) blast hole ABA sampling. It is imperative that on-site ABA analytical work be conducted. The optimum ABA sampling procedure and analytical method(s) would be carried out in the initial months of mine operation.

Imperative Costs

It should be emphasized that waste rock is dependent on the cutoff grade at the time of feasibility. The cutoff grade can vary with economics, and hence waste rock can vary over time, which will affect the ARD model. Low-grade-ore “waste rock” may become minable with rising commodity prices. This will affect the amount of waste rock that will go to the waste rock dump, with some becoming low-grade

material going to the mill, which in turn will affect the dump site and tailings material disposal. The movement and disposal of waste material is a major cost to the mine operator and as such must be strictly controlled. The long-term effect of monitoring waste rock as to acid rock drainage impact will have a major bearing on the overall economics of the mine. Thus, the ARD waste rock model must be updated continually.

Conclusions

Waste rock modeling must be an integral part of a geostatistical resource estimate study. The ability to characterize each waste block as AG, PAG, PAC, and/or PN in the block model is of importance for mine planning, pit wall characterization, and waste rock disposal. This information can also be used in predictive water flow chemistry models. A waste rock ARD prediction, disposal, and inventory scheme should be established by knowing the potential resource. This scheme must take into account the mine geology, blast hole cuttings (rock types, carbonate content by acid and staining tests, estimated sulfide content), and analytical results of drill and blast hole data. The scheme operates on input from the mine geologists who are responsible for the geological field input and decision(s) together with the analytical results from the mine assay laboratory. A computerized decision model can be built based on rules, hypotheses, and common sense, leading to logical relationships or concepts. The site waste rock ABA data must be reconciled with the ABA modeled for the waste blocks to determine the accuracy of the original prediction and whether or not the waste blocks modeled are correct. This reconciliation should be carried out yearly.

References and Suggested Reading

Bennett, M.W., Kempton, H.J., and Maley, J.P., 1997. Applications of geological block models to environmental management. In: 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 293–303.

Bursey, G.G., Mahoney, J.J., Gale, J.E., Dignard, S.E., Napier, W., Reihm, D., and Downing, B.W., 1997. Approach used to pit filling and pit lake chemistry on mine closure, Voisey's Bay, Labrador. In: 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 257–275.

Claridge, P.G., and Downing, B.W., 1993. Environmental geology and geochemistry at the Windy Craggy massive sulphide deposit, north-western British Columbia. CIM Bulletin, vol. 86, no. 966, pp. 50–57.

Day, S., 1995. Summary Notes. MEND Prediction Workshops, December, 7–8, Noranda Technology Centre, Pointe-Claire, QC, Canada.

Downing, B.W., 1999. Quality assurance and quality control. See ARD website, www.enviromine.com/ard.

Downing, B.W., and Giroux, G., 1993. Estimation of a waste rock ARD block model for the Windy Craggy massive sulphide deposit, northwestern British Columbia. Exploration and Mining Geology, vol. 2, no. 3, pp. 203–215.

Downing, B.W., and Madeisky, H.E., 1997. A lithogeochemical method for acid rock drainage prediction. Presented at the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, 16 pp.

Downing, B.W., and Madeisky, H.E., 1999. Lithogeochemical methods for acid rock drainage studies and

prediction. Exploration and Mining Geology, Vol. 6, no. 4, pp. 367–379.

Thrush, P.W., et al., 1968. Dictionary of Mining, Mineral and Related Terms. U.S. Bureau of Mines Special Publication. Department of the Interior, Washington, DC, 1269 pp.

24
Lithogeochemical Methods for Acid Rock Drainage Prediction

BRUCE W. DOWNING AND HANS E. MADEISKY

The acid rock drainage (ARD) buffering capacity of mine waste is governed by its bulk chemical composition and its mineral assemblage. Conventional acid–base accounting (ABA) tests can be used to predict short-term buffering but should be used with caution to model or predict the long-term ARD buffering capacity of mine waste.

Introduction

ABA data for mine waste samples from four different deposit types—anorthosite-hosted magmatic sulfide nickel, dunite-hosted magmatic sulfide nickel, porphyry copper–gold, and volcanic-hosted high-sulfidation epithermal silver—have been compared with whole-rock geochemical and petrographic data obtained from the same samples. The data were compared with whole-rock geochemical and petrographic data obtained from the same samples. Our objective was to devise and test a method of predicting ARD buffering capacity based on bulk chemistry and modal mineralogy. In other words, we developed a quantitative theoretical method for calculating neutralizing potential, relying on easily obtainable and relatively inexpensive whole-rock and sulfur x-ray fluorescence (XRF) analyses, which could substitute for conventional ABA procedures in situations where these procedures are either too costly or too time consuming.

For each deposit type, models were devised that reasonably approximate the net neutralization potential estimated by the ABA data obtained from laboratory tests. Once an appropriate model has been developed and tested, portable XRF equipment, already in use for grade control at many mine sites, could provide the whole-rock and sulfur analyses required to estimate the ARD potential of the waste material. Although this approach is not intended as a substitute for the legally mandated ABA test procedure, it could facilitate the timely and cost-effective management and mitigation of ARD at a mine site (Downing and Madeisky, 1999).

The basic questions to ask of ARD prediction work are:

1. What controls ARD?
2. What controls bulk chemistry?
    a. Visual mineralogy (hand sample scale)
    b. Petrographical studies (thin-section scale)
    c. Lithogeochemistry (chemical scale)
3. Can we model the destruction of rock-forming minerals?
    a. In fine-grained rocks
    b. In altered rocks
    c. In metamorphosed rocks

4. Can we model lithogeochemistry and ARD?

Methodology

Acid–base accounting data for mine waste samples from four different deposit types were examined:

- Anorthosite-hosted magmatic sulfide nickel
- Dunite-hosted magmatic sulfide nickel
- Porphyry copper–gold and volcanic-hosted high-sulfidation epithermal silver

Testing included:

- ABA BC Research, Inc. method
- Initial pH
- Total sulfur (Leco)
- Sulfate-sulfur (turbidimetric method)

Whole-rock analyses [inductively coupled plasma emission spectroscopy (ICP-ES) using lithium metaborate fusion] provides major oxide data, provides bulk chemistry analyses (total inorganic carbon), and provides carbonate content sampling assay pulps of core collected from exploration drilling and grab samples collected from outcrop. Samples represent altered and unaltered host rocks, both barren and subore, collected specifically to determine the limits of ABA for acid-generating and non-acid-generating material.

Sample pulps from one of the deposits were composited to represent lithologic types and over mining bench heights to represent mining blocks. Samples at the silver deposit were collected from outcrops, and had their weathering rinds cut away.

Petrographic studies are performed:

- To determine modal mineralogy for rock classification (as a check on field classification)
- To examine sulfide mineralogy
- To determine primary and secondary mineralogy and alteration variation that would affect the determination of the neutralization potential.
- To determine the degree of partitioning of feldspars into calcic sodic and potassic end-members which may have a bearing on the silicate-based buffering capacity of these rocks.

Lithogeochemical studies are performed:

- To determine the bulk chemistry of the waste rock; to classify rock types and alteration facies
- To test CIPW normative mineralogy
- To correlate chemistry with petrographic studies
- To determine whether and to what extent alternative methods could be developed for conventional ABA analytical procedures
- To determine complementary prediction methods and models in conjunction with conventional or legally mandated net neutralization potential (NNP) and neutralization potential–acid production

(NPR) methods.

Rock and Alteration Lithogeochemistry

Lithologic Variation

Rock types can be distinguished geochemically by their conserved element ratios. A diagnostic property of rocks belonging to the same rock type or the same cogenetic group is that they share a common conserved element ratio no matter how metamorphosed or weathered these rocks might be. Conserved elements are those that do not participate in mass transfer either in rock-forming or alteration processes. In igneous rocks such elements are incompatible in the melt and are effectively immobile in hydrothermal fluids. The loss of alkali cations from rocks (i.e., the degree of alkali depletion) can be measured by residuals to linear molar covariation models. The degree of H^f substitution (i.e., degree of hydrolysis of these rocks) can be estimated by the initial pH of a rock–water slurry measured as part of conventional ABA.

To test for the presence of conserved elements, concentrations of two elements are plotted on an *x*–*y* scatterplot (see Figure 24.1). Where lines can be drawn through a linear array of data points and the origin of the plot (within the limits of analytical error), the samples can be considered as belonging to one rock type, and the two elements can be considered to be conserved. (In most of the figures, the data reported in weight percent have been converted to molecular proportions to construct linear covariation models that relate the data to mineral formulas and chemical reactions and, specifically to relate changes in the analytical data to changes in the modal mineralogy of the rocks.)

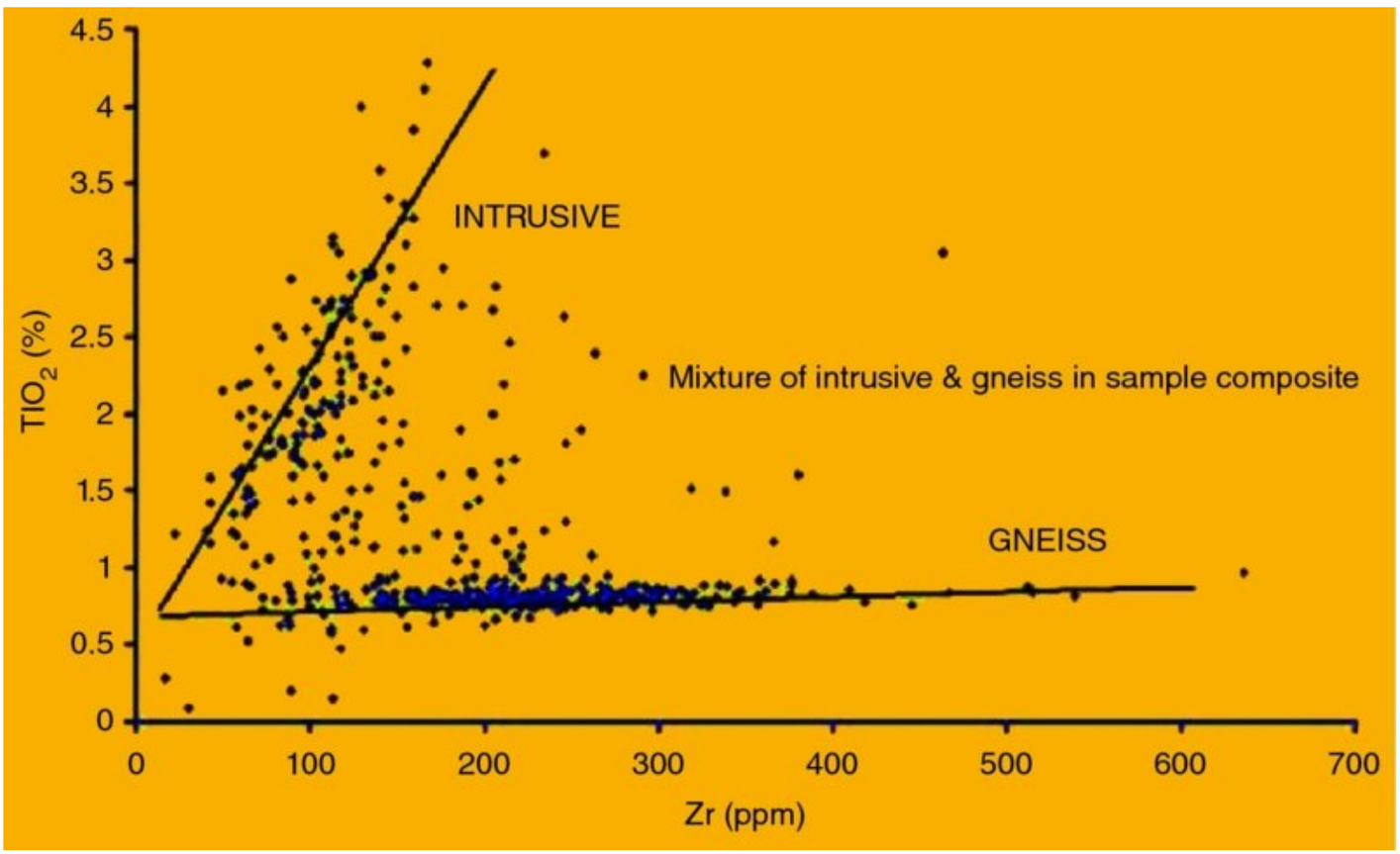


Figure 24.1 Rock type classification (MMS data set). Lithogeochemical methods for ARD prediction: alteration type of classification using the feldspar–biotite model.

It is important to keep in mind that the lines drawn through the origin of the scatterplot are constant-ratio lines they are not regression lines. On the scatterplot of TiO_2 versus Zr (Figure 24.1), two distinct lithological populations can be distinguished; the intrusives are identified by the higher conserved element ratio, and the gneisses are characterized by a linear trend approximately parallel to the *x*-axis. Ti and Zr are conserved elements in the intrusives; in the gneisses Ti is probably not conserved. Other plots that can be used to corroborate these observations are: Al_2O_3 versus Zr, Nb versus Zr, and Y versus Zr (not shown).

Alteration

When rocks become hydrothermally altered or weathered, their bulk chemistries and modal mineralogies change, and consequently their NPs change. See Figure 24.2, where a magmatic sulfide nickel deposit is hosted in mafic intrusives and mafic-derived hornblende gneisses. The appropriate lithogeochemical model for these rocks is the three-phase petrologic model for mafic rocks (¼Al + ½Fe + ½Mg + 1½Ca + 2¾Na)/Zr versus Si/Zr. This model is based on the bulk stoichiometric covariation of Al, Fe, Mg, Na, and Na with Si in the rock-forming silicates olivine [$(Fe, Mg)_2SiO_4$], clinopyroxene [$Ca(Fe, Mg)Si_2O_6$], and plagioclase ($CaAl_2Si_2O_8$) in ultramafic and mafic rocks. On this model unaltered rocks plot along the model line of slope 1; if the rocks contain hornblende, they plot below that line, depending on the composition of hornblende and on how much is present. Altered rocks plot below or to the right of the model line, depending on whether they have lost Ca and Na or have gained Si, respectively. In the figure, the mafic intrusive (anorthosite gabbro) plots along the model line of slope 1, and the hornblende gneiss plots along a model line of slope 0.75. The fact that these samples plot along, and not too far away from, these two model lines suggests that these rocks are unaltered; the scatter of samples between the two model lines is probably due to the compositing of rock types into mining blocks.

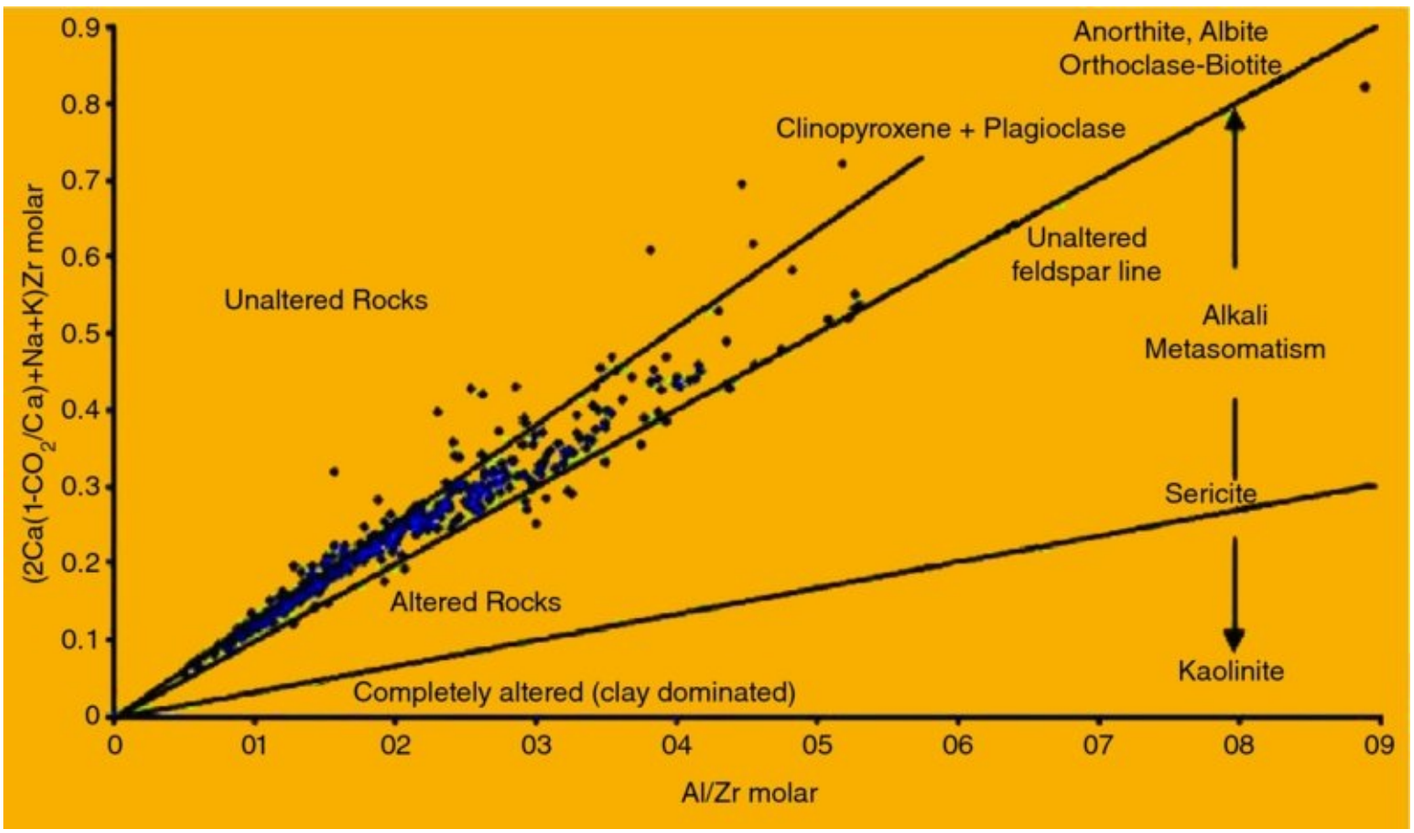


Figure 24.2 Alteration type of classification using the feldspar–biotite model (MMS data set).

The main metasomatic process associated with host rocks of hydrothermal sulfide deposits is the loss of Ca, Na, and (to a lesser extent) K cations from rock-forming minerals. In hydrothermally altered rocks the lost cations are replaced by both H and K ions, resulting in a modal mineralogy dominated by micas and clays, whereas in weathered rocks these cations are substituted mainly by H ions, leading to a clay-dominated modal mineralogy. A useful model for dealing with unaltered and altered igneous rocks and feldspathic sedimentary rocks is the feldspar–biotite model (2Ca + Na + K)/Zr versus Al/Zr, which is based on the stoichiometrically defined covariation of the sum of the alkalis with aluminum in anorthite ($CaAl_2Si_2O_8$), albite ($NaAlSi_3O_8$) orthoclase ($KAlSi_3O_8$) and biotite [$K(Fe, Mg)_3AlSiO_{10}(OH)_2$]. Unaltered intermediate to felsic rocks plot on the model line of slope 1, regardless of their actual feldspar compositions or feldspar–biotite mixing proportions. Altered rocks can plot above or below this model line, depending on whether they have gained or lost alkalis in the alteration process. Since Al is generally immobile in hydrothermal fluids, rocks plotting below the model line are interpreted to have undergone alkali loss, while felsic rocks plotting above the model line are interpreted to have experienced carbonate alteration. Rocks plotting on the line with slope ⅓ are fully sericitized, and rocks plotting on the *x*-axis have completely lost their alkalis (e.g., advanced argillic alteration due to acid leaching). For any sample that plots below the model line, the extent of alkali loss can be measured by its relative residual which is calculated by taking the slope of the line through the sample and the model line intercept (in this case a line through the origin) and subtracting this slope from the model line slope.

This model is sensitive to carbonate metasomatism because Ca must be included in the sum of the alkalis. For example, in many epithermal environments the lateral margins and hanging wall of the alteration zone host calcite veins. Carbon dioxide analyses are required to accommodate the effect of carbonate alteration. To deal with carbonate-altered rocks, the *y*-axis term of the model above is modified. For rocks whose CO_2/Ca molar ratios are greater than 1, the *y*-axis term $[2Ca(1 - CO_2/Ca) + Na + K]/Zr$ is used. For rocks whose CO_2/Ca molar ratios are less than 1, the *y*-axis term (Na + K)/Zr is used instead, assuming that all of the Ca in the rock has been taken up by metasomatic carbonates.

Figure 24.3 is a plot showing alteration facies from unaltered to extremely altered felsic volcanics; here a few samples plot along the model line, but most of the samples plot below this line, indicating that they have undergone alkali depletion. The mineralized samples, those that contain sulfides, plot near the sericite line, while the fully alkali depleted samples plot along the *x*-axis; these are the samples that contain no alkalis, probably as a result of extreme acid leaching. Because all the mineralized samples are alkali-depleted, they are not likely to be good buffers for ARD reactions. The buffering capacity of these rocks is directly related to alteration facies and decreases steadily from fresh to advanced argillic-altered rock.

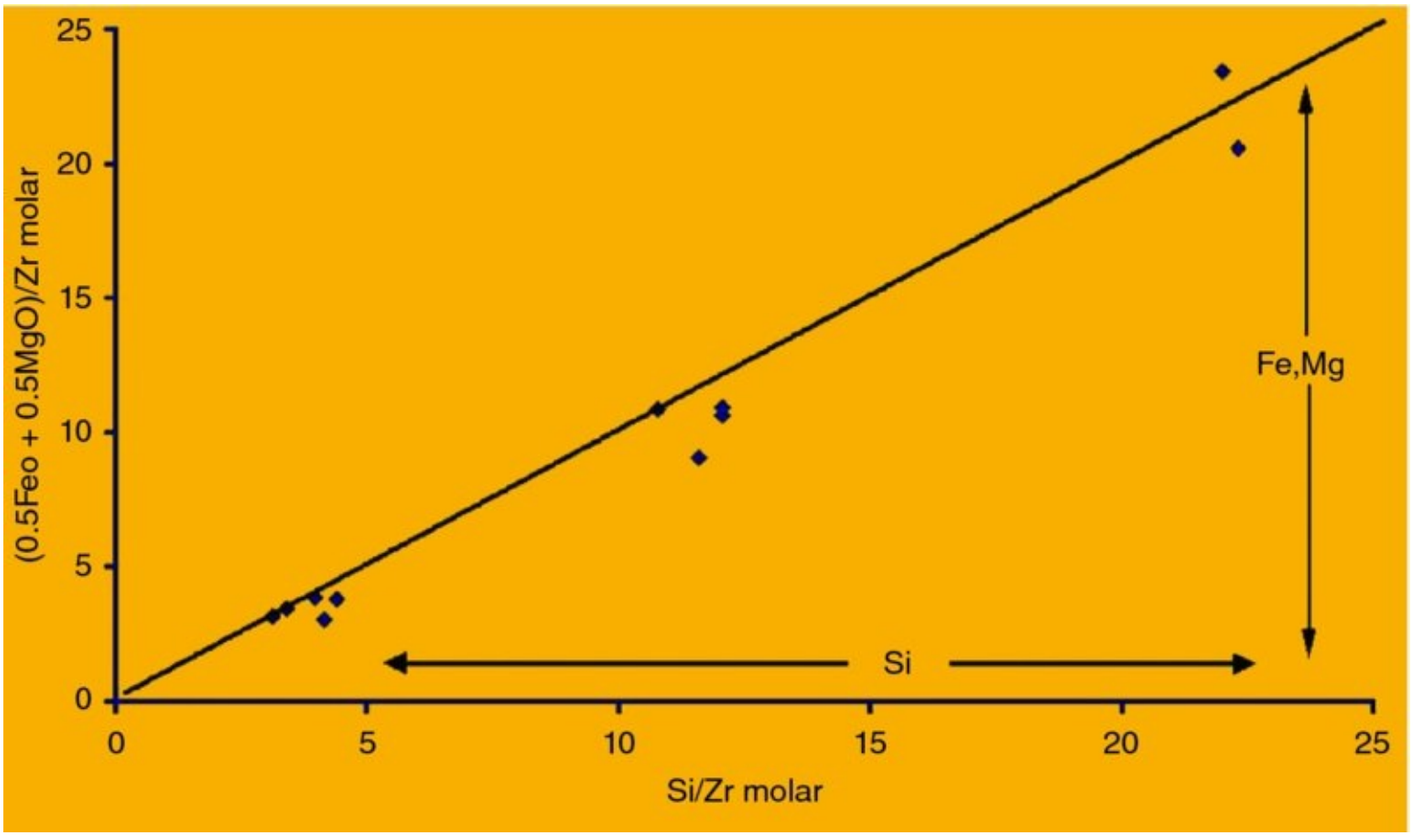


Figure 24.3 Olivine fractionation [crystal model (MI)S data set].

The weathering potential index

$$\mathrm{WPI} = \frac{100 \times \mathrm{moles}(\mathrm{CaO} + \mathrm{Na_2O} + \mathrm{K_2O} + \mathrm{MgO})}{\mathrm{moles}(\mathrm{SiO_2} + \mathrm{Al_2O_3} + \mathrm{Fe_2O_3} + \mathrm{CaO} + \mathrm{Na_2O} + \mathrm{K_2O} + \mathrm{MgO})}$$

Assessment of the manner and rate of deterioration of the rock matrix in the field. Abrasion pH is a function of a rock's modal mineralogy; OR is an indicator of a rock's weathering potential. The WPI versus initial pH scatterplot (Figure 24.4) data set shows that there is a functional relationship between the weathering potential of the samples and their initial pH. The basis of this relationship is the modal mineralogy of the rocks. As these rocks become more and more altered, they lose progressively more alkalis, while their Al content remains approximately constant. Thus, the bulk alkali/aluminum ratio of these rocks decreases and the mineralogy of the altered rocks becomes dominated first by micas and then by clays. Since micas and clays behave like acids in water, the initial pH as well as the abrasion pH of these rocks will decrease as the abundance of micas and clays increases.

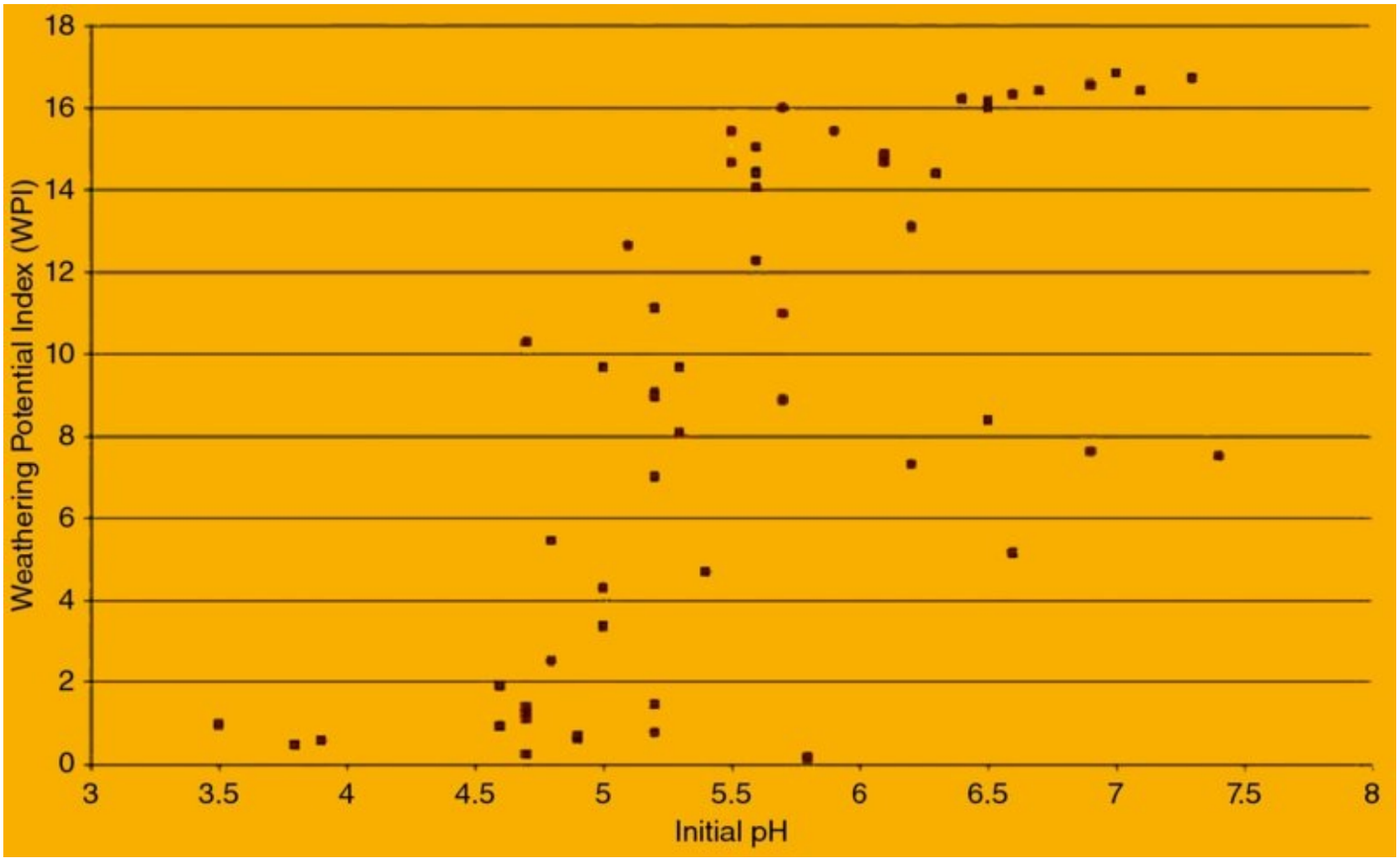


Figure 24.4 Weathering potential index versus initial pH (SFV data set). Lithogeochemical methods for ARD prediction: acid consumption versus time.

CIPW Normative Calculations

NewPet software is used to perform CIPW normative calculations [Named after the authors of a well-known article (Cross et al., 1902)], which estimate the modal mineralogy of these rocks. The modal mineralogy Predicted (i.e., the mineral proportions calculated by the CIPW computer program) were found to differ markedly from the modal mineralogy observed. Calculation of CIPW norms and mesonorms is limited to modeling unaltered rocks, and mesonorm can accommodate the presence of biotite and hornblende, but neither procedure can deal with the presence of alteration and sulfides. Normative and not-so-normative calculation algorithms differ for saturated versus undersaturated rocks; thus, the appropriate algorithm must be chosen for a specific lithology. When altered rocks are present, CIPW normative calculations cannot produce reliable estimates of mineral abundance and thus cannot support meaningful NP estimates.

Neutralization Capacity

Reactivity of Gangue Minerals

For ABA analyses the reaction rate is an important factor in assessing the results of acid–rock interaction over long periods of time. A plot of acid consumption versus time for four samples is shown in Figure 24.5. This plot indicates that some rocks will be acid buffering much sooner than others; in other words, the plots show bulk reaction rates for each sample under laboratory conditions. The slope of each curve is a measure of the bulk reaction rate for that sample, and the inflection points on each curve probably

indicate the influence of different mineral species on the buffering reactions. These curves can be classified by their slopes as to fast and slow rates of weathering and/or acid buffering.

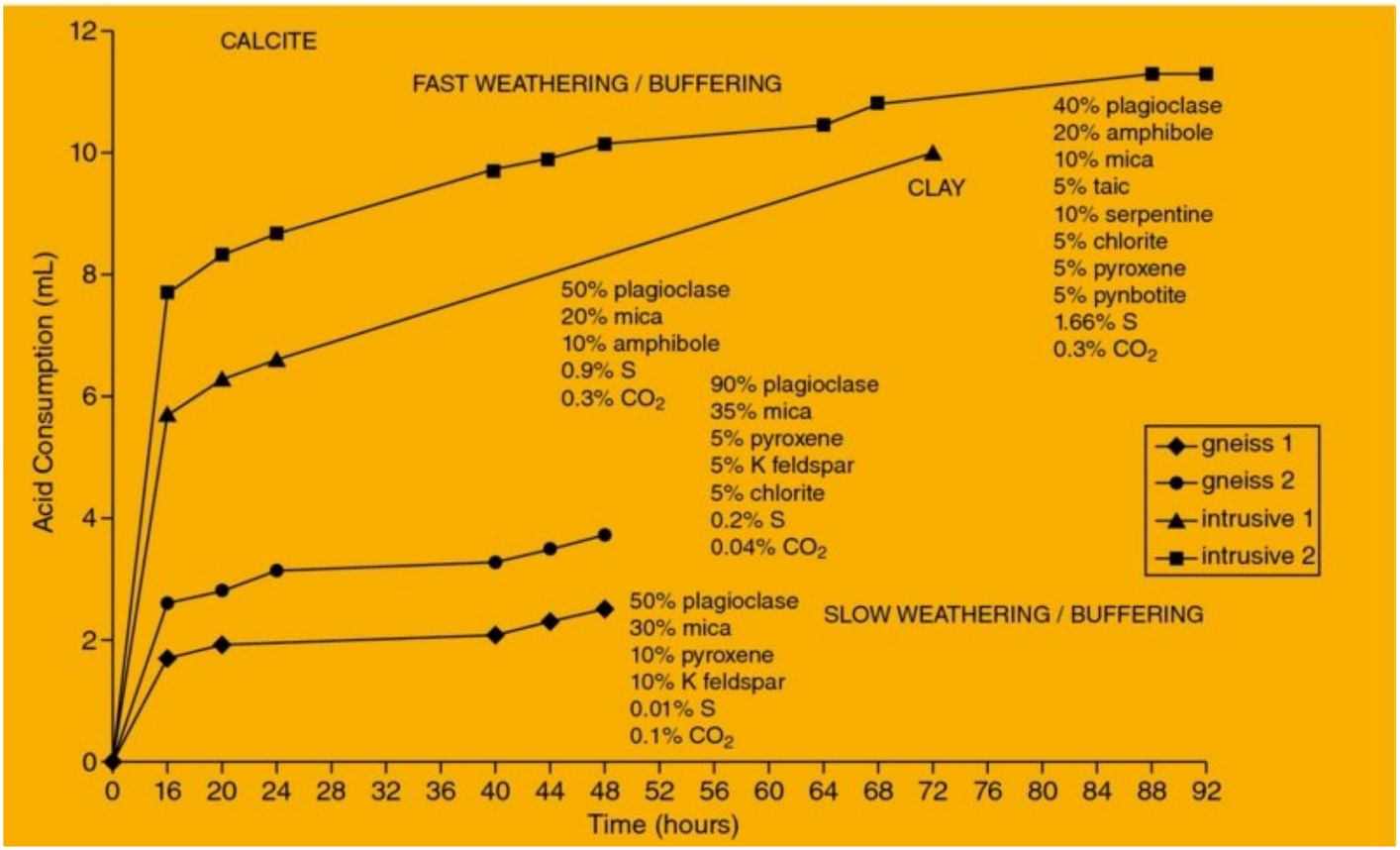


Figure 24.5 Acid consumption versus time (MMS data set). Lithogeochemical methods for ARD prediction: neutralization potential versus time for the NBM-1 standard.

A plot of acid consumption (calculated NP) versus time typically shows a sharp initial rise as calcite is being consumed, then a lower rise due to Mg–Fe carbonates and/or Mg–Ca silicate dissolution, then another steeper rise when clays and phyllosilicates begin to break down and participate in the buffering reaction. NP tests should probably be run for a minimum of two to four weeks to properly estimate the actual NP of waste material. The buffering rates of individual samples (representing waste blocks) can be classified as slow, intermediate, and fast, using the minima, maxima, and inflection points of their respective curves (see Figure 24.5). These rates can then be used to map the predicted buffering rates of waste blocks in a mining bench. A similar plot of NP versus time is shown for the NBM-1 standard in Figure 24.6. The net buffering capacity of a waste block is the product of the relative abundance and reaction rate of the neutralizing minerals calcite, Mg–Fe carbonates, Fe–Mg silicates, alkali silicates, phyllosilicates, and clay.

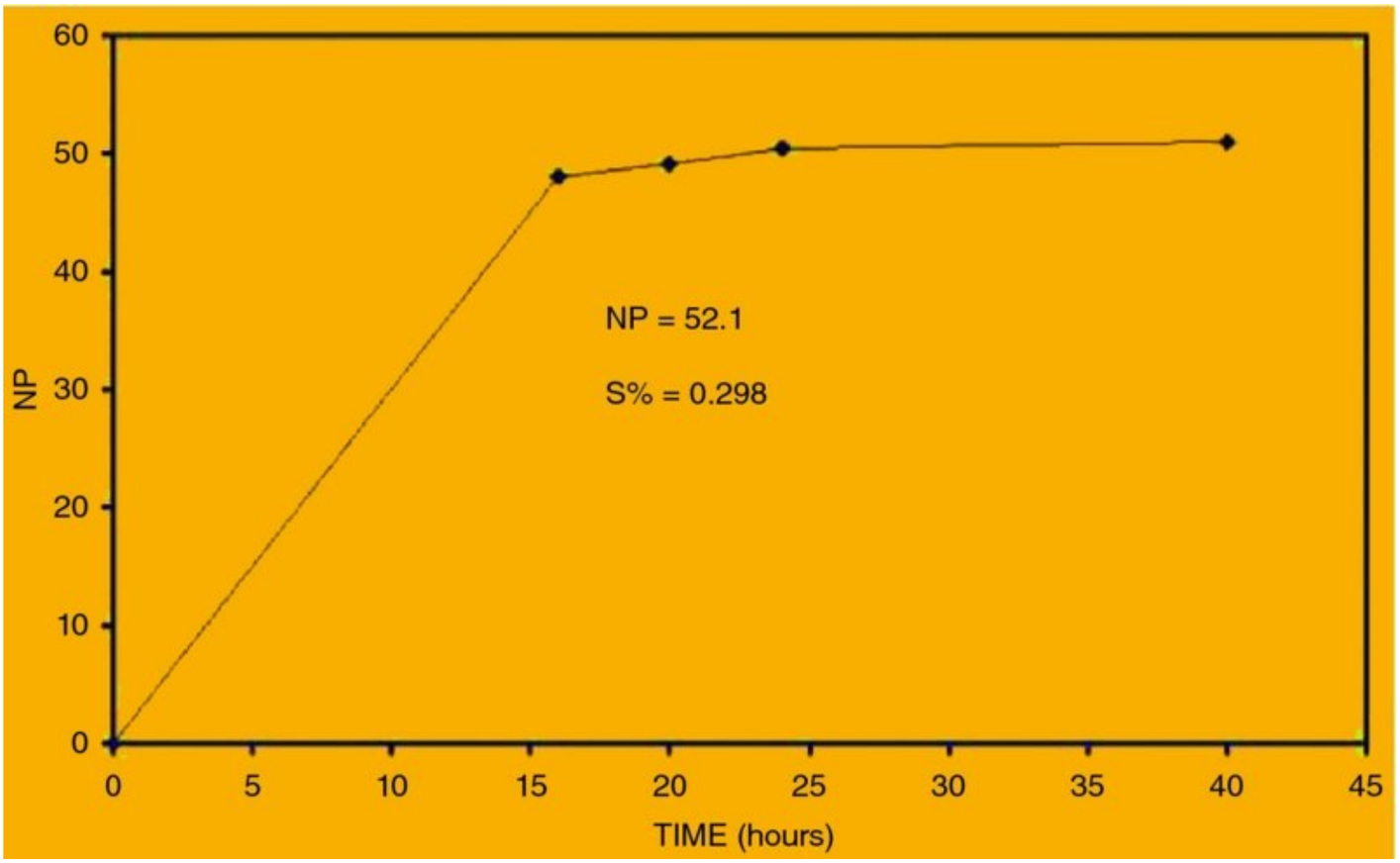


Figure 24.6 Neutralization potential versus time for the NBM-1 standard.

Surface Area of Minerals Available for Reaction

Particle size is very important. In a typical ABA test, samples are ground to approximately −150 mesh. At this particle size the reaction surface areas of most rock-forming silicates and of carbonates are approximately the same, but the reaction surface areas of micas and clays can be several orders of magnitude greater. Clay minerals originally present in mine waste, along with the clays formed by acid-leaching the rock-forming silicates, will probably dominate the long-term water–rock interactions and thus the long-term neutralization potential and the adsorption of metals liberated by the ARD process.

Flow Rate of Acidic Iron-Bearing Solutions

The flow rate of acidic iron-bearing solutions relates primarily to the time during which the solution is in contact with various minerals. The effective neutralizing power of a gangue or rock is the product of these factors distinguishing it from the theoretically total neutralizing power that the gangue or rock would possess if the acid remained in contact with a given unit area long enough for the gangue to react fully. The neutralizing power that has been calculated via the BCR method is only a measure of the initial neutralization power.

Lithogeochemical Models of Neutralization Potential

Sulfide-Sulfate Model

To model the ARD buffering capacity of rocks, consider which sulfate minerals are likely to be formed by the reaction of sulfuric acid (H_2SO_4) with the minerals present in these rocks. Given the abundance of Ca-

and K-bearing silicates in rocks, the minerals most likely to form are gypsum [$CaSO_4 \cdot 2(H_2O)$], anhydrite ($CaSO_4$), and alunite [$KAl_3(SO_4)_2(OH)_6$] or the intermediate product jarosite [$KFe^{3+}(SO_4)_2(OH)_6$]. The ability of Mg to buffer ARD is also important, especially in Mg-rich rocks such as ultramafics. The end products of ARD buffering in most other rocks (gypsum, anhydrite, and alunite) can be modeled by plotting the molar ratios S_{total}/Zr versus (Ca+0.5K)/Zr. Because Zr is a conserved element, it can be used in the denominator to normalize the data. The molar ratio $S_{total}/(Ca + ½K)$ describes the theoretical buffering capacity of these rocks based on balanced molar quantities of S, Ca, and K in the sulfate minerals.

$S_{total}/(Ca + ½K)$ can be considered equivalent to AP/NP in a theoretical sense; however, this buffering model is based on bulk chemistry, irrespective of the abundance or reactivity of neutralizing minerals present in the rock, whereas NP is an empirical (titration) measurement of the contribution that soluble neutralizing minerals make to ARD buffering in the test tube. Therefore, the empirical measurements are typically much lower than the theoretical predictions.

On this linear covariation model (Figure 24.7), sulfide minerals plot along the *y*-axis, the sulfate minerals gypsum, anhydrite, and alunite plot along the model line of slope 1, and Ca- and K-bearing silicate minerals plot along the *x*-axis. Samples plotting along the sulfate model line, $S_{total}/(Ca + ½K) = 1$, should be ARD neutral; samples plotting above the model line, $S_{total}/(Ca + ½K)$ greater than 1, should be acid generating; and samples plotting below the model line, $S_{total}/(Ca + ½K)$ less than 1, should be acid buffering. This ratio can be considered equivalent to AP/NP in a theoretical sense, however, this buffering model is based on bulk chemistry, irrespective of the abundance or reactivity of neutralizing minerals present in the rock, whereas NP is an empirical (titration) measurement of the contribution that soluble neutralizing minerals make to ARD buffering in the test tube. Therefore, the empirical measurements are typically much lower than the theoretical predictions.

Net Neutralizing Potential Model

Theoretical NNP versus Measured NNP

The maximum theoretical NNP can be stated by the equation NNP = (Ca + ½K) − S. Short-term net buffering capacities (NBCs) consider ARD buffering by carbonate minerals with high reaction rates, and long-term NBCs consider buffering by silicate minerals with much slower reaction rates. The difference in slope and intercept of the trend observed in the data and the trendline predicted (intercept 0,0 and slope = 1) is a measure of the factor (or amount) by which the neutralizing potential actually available in these rocks is overstated. The theoretical capacity far exceeds the actual ability of these rocks to buffer the ARD reactions, as simulated by the ABA tests.

NNP graphs of theoretical and model NNP can be developed whereby short- and long-term buffering effects are accounted for by using major oxide data. These graphs are based on the premise that the bulk oxide data are representative of the bulk mineralogy of a rock, and that NP determinations are a result of mineralogical buffering. The theoretical NNP expresses the maximum capacity of a rock to buffer an ARD reaction given its bulk chemistry, and as such is independent of pH-dependent titration analyses such as NP.

Because conventional NP measurements are conducted over relatively short time periods, and because these measurements tend to be biased in favor of the nearly instantaneous reaction of H_2SO_4 with Ca-bearing carbonates such as calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$], when they are present, two

NBCs should be considered: a short-term NBC that considers ARD buffering by carbonate minerals with high reaction rates and a long-term NBC that considers buffering by silicate minerals with much slower reaction rates. In the laboratory, buffering by carbonates is obvious enough by the liberation of CO_2 from the test tube (fizzing), whereas evidence of the role of silicate minerals in buffering in the form of alkali-depleted aluminosiicate minerals (hydrous micas and clays) must be confirmed by mineralogical (x-ray diffraction) analysis of the solid residue remaining in the test tube.

The maximum theoretical NNP can be stated by the equation NNP = (Ca + ½K) − S. A plot of the theoretical NNP versus measured NNP (Figure 24.8) shows a strong linear trend and suggests a link between the theoretical and empirical data. The difference in slope and intercept of the trend observed in the data and the trendline predicted (intercept 0,0 and slope = 1) is a measure of the factor (or amount) by which the neutralizing potential actually available in these rocks is overstated. The distribution of data indicates that there is a correlation but that data points at or near the origin show some scatter, as would be expected, as the Ca + ½K represents total buffering (neutralizing) capacity while NP represents only partial buffering capacity by soluble minerals measured over a very short time. However, when comparing the theoretical buffering capacity with the measured net neutralization potential (NNP) of rocks, it becomes quite clear that the theoretical capacity far exceeds the actual ability of these rocks to buffer the ARD reactions as simulated by the ABA bench tests. The problem is that the unaltered rocks, which have significant amounts of Ca and K to contribute to buffering ARD, contain feldspars which do not break down rapidly enough to react with and buffer the H_2SO_4 being generated by the oxidizing sulfides, and the altered rocks, which contain micas and clays, may break down quickly enough but do not contain sufficient Ca and K to buffer the ARD reaction.

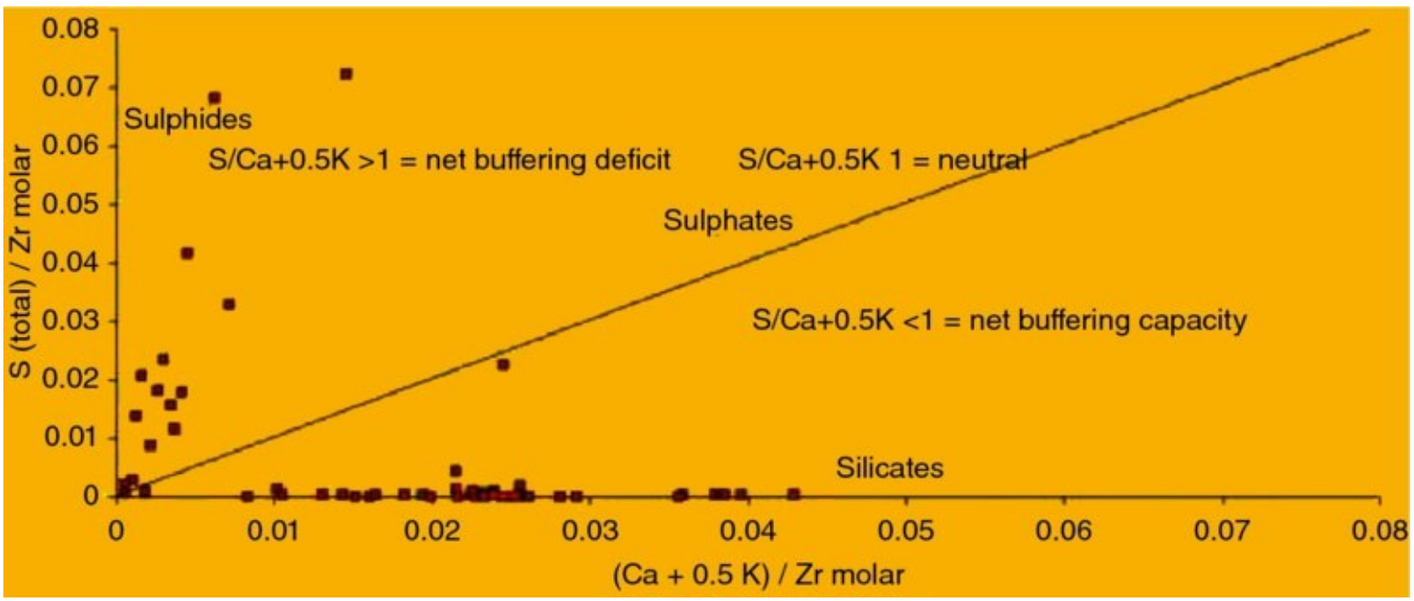


Figure 24.7 Theoretical buffering capacity (SFV data set). Lithogeochemical methods for ARD prediction: theoretical NNP versus measured NNP.

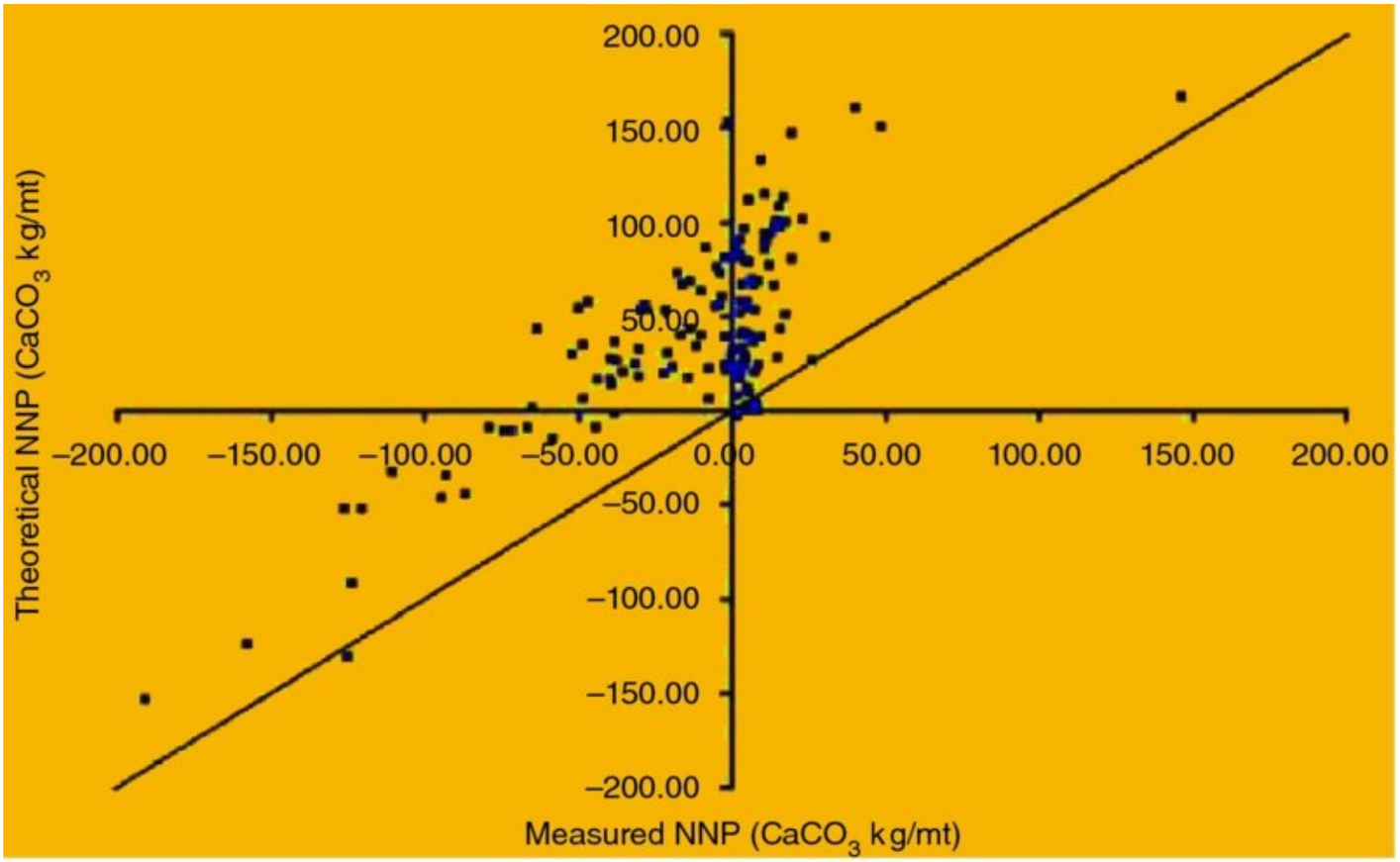


Figure 24.8 Theoretical versus measured NNP (PCG data set).

Theoretical NNP can be refined further by modeling the data after examination of petrographic data and by plotting CO_2 versus NP. If a significant amount of carbonate minerals is present and the CO_2 versus NP data show a strong correlation, CO_2 must be taken into account in the equation. When modeled (i.e., when carbonate minerals are taken into account) the data from Figure 24.8 produce a very good correlation, as indicated by the data points fitting a line of slope 1 (see Figure 24.9).

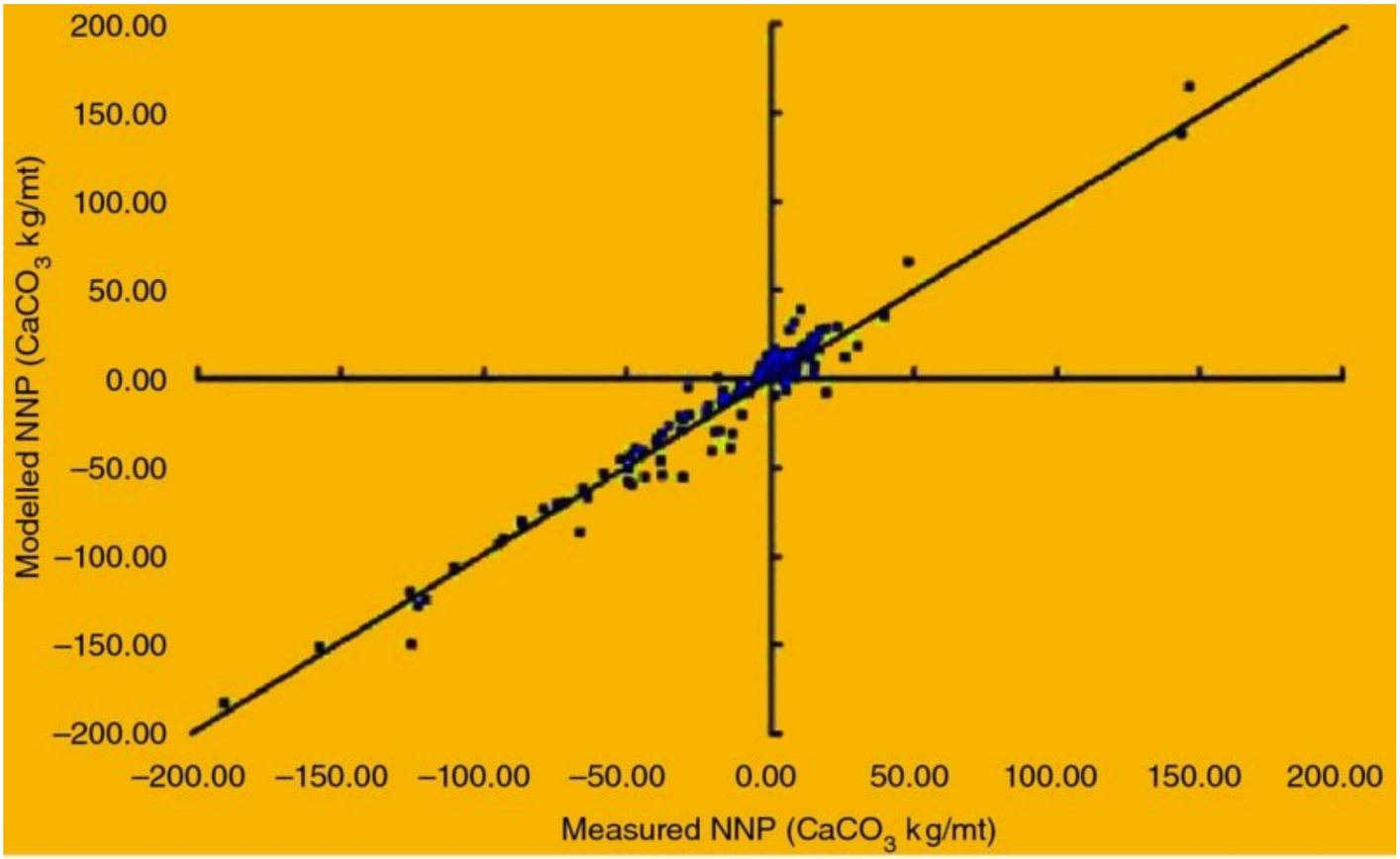


Figure 24.9 Modeled versus measured NNP (PCG data set).

Refinement of the NNP Model

Examine the relationship of initial pH and alteration using the alkali depletion index. Once a functional relationship between alkali/aluminum ratios and initial pH has been established (Figures 24.10 and 24.11), an equation relating alkali/aluminum molar ratios to initial pH can be substituted for the initial pH measurements in the lithogeochemical NNP model. This means that all of the data necessary for calculating the model can now be obtained directly from whole-rock analyses.

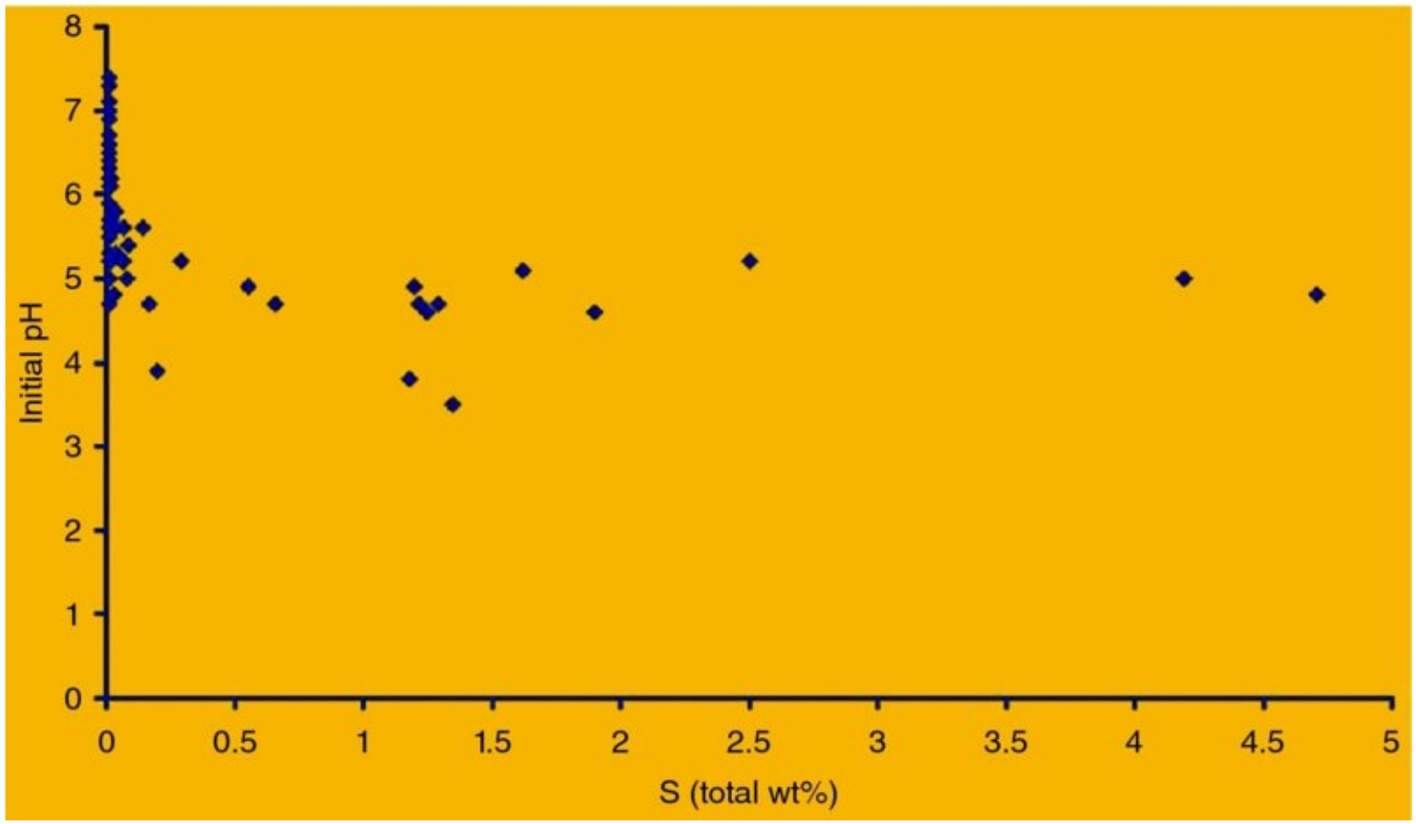


Figure 24.10 Initial pH versus total percent sulfur (SFV data set).

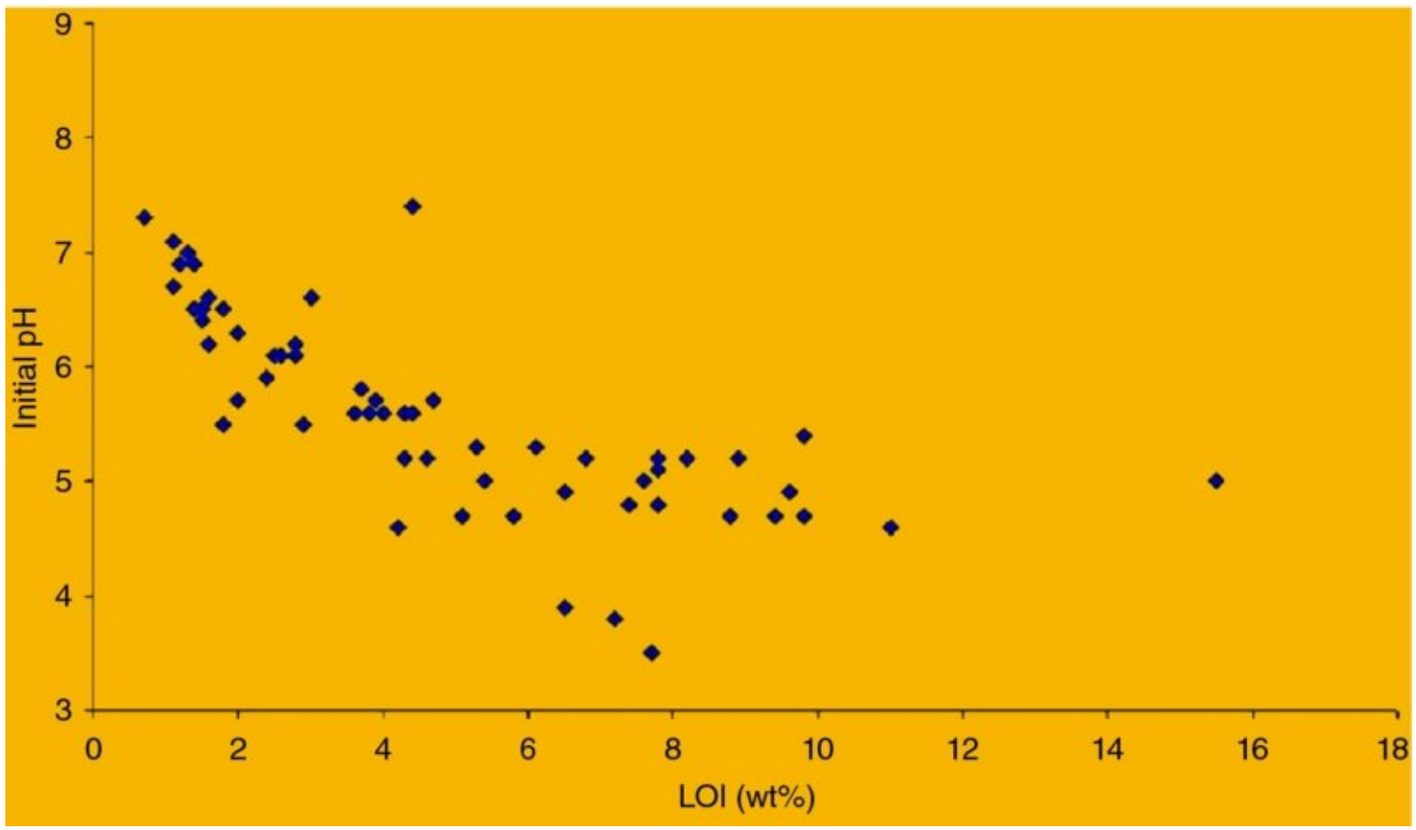


Figure 24.11 Initial pH versus loss on ignition (SFV database).

It is widely believed that the initial pH of a water–rock slurry is controlled by the sulfide mineral content of the rocks. The measurements and analytical data from the high-sulfidation epithermal silver deposit

provide an excellent demonstration that, at least in this case, this is not so. A plot of the initial pH versus S_{total} content (Figure 24.10) shows that in these rocks there is no correlation between initial pH and S_{total}. What is evident, however, is that only rocks with initial pH values lower than 5.5 contain any S at all, and that in these rocks S_{total} concentrations vary from 0.0 to nearly 5.0 wt%. What controls the initial pH of these rocks can be observed on the plot of initial pH versus loss on ignition (Figure 24.11). Because they contain little or no CO_2, loss on ignition in these rocks is a reasonably good approximation of their degree of hydrolysis: the substitution of H for Ca, Na, and K cations in feldspars, which results in a mica- and clay-dominated modal mineralogy. The reason that the initial pH is low in rock–water slurries containing abundant clays and/or micas is that in water, these minerals tend to behave as acids (Grant, 1969). Whether or not these altered rocks also contain sulfides is of no consequence in terms of their initial pH values (see Figure 24.10). The relationship between the sulfur content and the initial pH of rocks is that although altered rocks have low initial pHs and sulfides are present only in altered rocks, not all altered rocks contain sulfides. Therefore, although initial pH cannot predict the presence or abundance of sulfide minerals, it is a reasonable predictor of alteration facies (e.g., alkali depletion) (see Figure 24.12). A comparison of modeled NNP values with measured NNP values (Figure 24.13) shows a very good correlation.

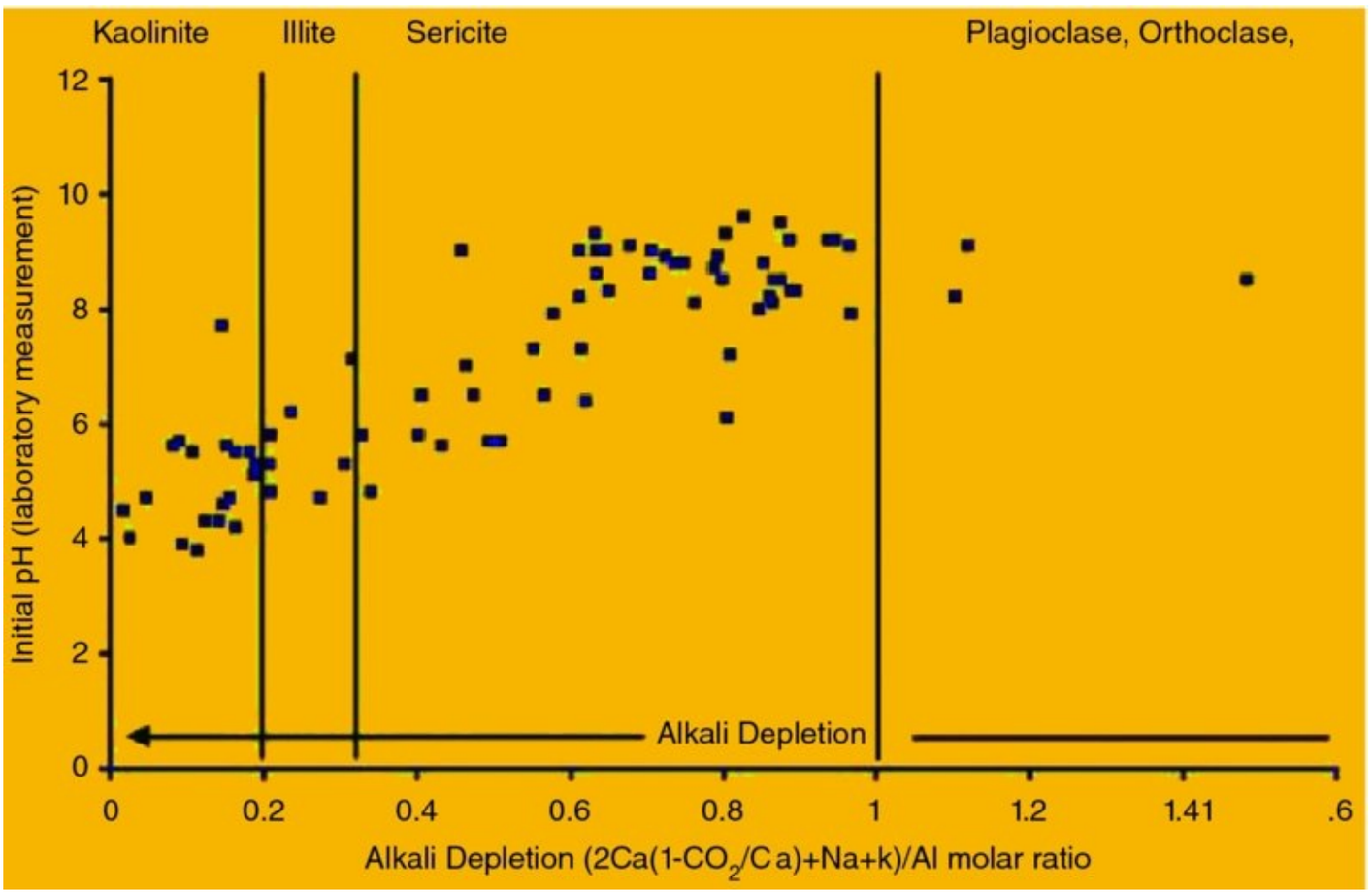


Figure 24.12 Initial pH versus alkali depletion (PCG data set).

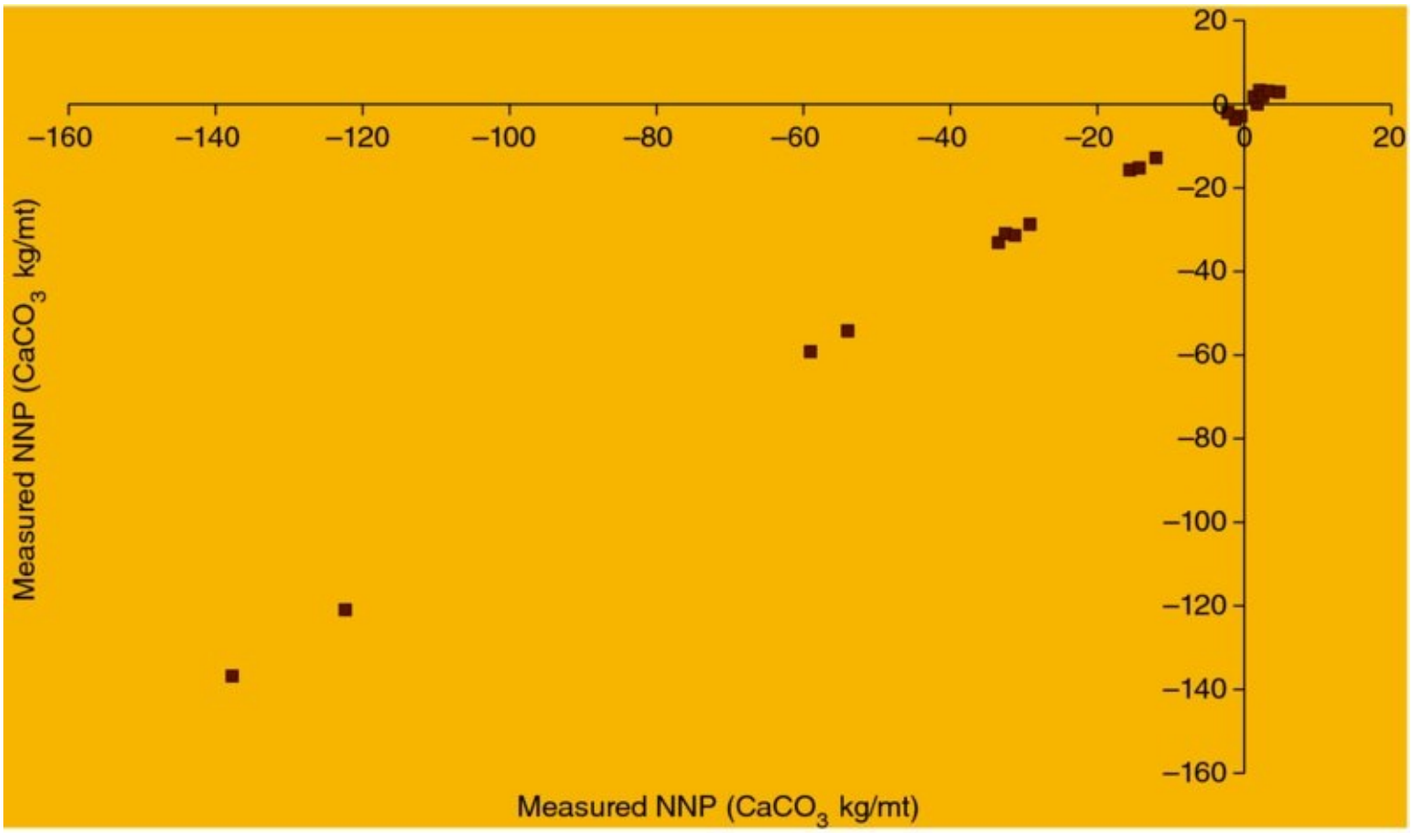


Figure 24.13 Modeled NNP values versus measured NNP values.

It appears that the initial pH of these rocks is more or less inversely proportional to the capacity of these rocks to contribute Ca and K to buffer the ARD reaction. In other words, the reaction rate of the Ca- and K-bearing minerals in these rocks can be expressed in terms of their initial pH and/or in terms of their degree of hydrolysis. Thus, initial pH can be used as a factor in a lithogeochemical model of the NNP of these rocks, which can be calculated using the series of equations that follow.

Lithogeochemical methods for ARD prediction:

$$\mathrm{NNP}(\mathrm{CaCO_3\ kg/mt}) = 1000.9\left[\frac{1}{\text{initial pH}}\left(\frac{\mathrm{CaO}}{56.08}+\frac{0.25\mathrm{K_2O}}{94.20}\right)-\frac{\mathrm{S_{total}}}{32.06}\right] \tag{24.1}$$

$$\mathrm{NNP}(\mathrm{CaCO_3\ kg/mt}) = 1000.9\left[\frac{1}{\text{initial pH}}\left(\frac{\mathrm{Ca}}{40.07}+\frac{0.5\mathrm{K}}{39.09}\right)-\frac{\mathrm{S_{total}}}{32.06}\right] \tag{24.2}$$

$$\mathrm{NNP}(\mathrm{CaCO_3\ kg/mt}) = 1000.9\left[\frac{0.15}{2(\mathrm{Alk/Al})+5}\left(\frac{\mathrm{CaO}}{56.08}+\frac{0.25\mathrm{K_2O}}{94.20}\right)-\frac{\mathrm{S_{total}}}{32.06}-0.0025\right] \tag{24.3}$$

$$\text{NNP}(\text{CaCO}_3\ \text{kg/mt}) = 1000.9\left[\frac{0.15}{2(\text{Alk/Al})+5}\left(\frac{\text{Ca}}{40.07}+\frac{0.5\text{K}}{39.09}\right) - \frac{S_{\text{total}}}{32.06} - 0.0025\right] \tag{24.4}$$

$$\text{Alk/Al molar ratio} = \frac{\frac{2\text{CaO}}{56.08}+\frac{2\text{Na}_2\text{O}}{61.98}+\frac{2\text{K}_2\text{O}}{94.20}}{2\text{Al}_2\text{O}_3/102.96} = \frac{\frac{2\text{Ca}}{40.07}+\frac{\text{Na}}{22.98}+\frac{\text{K}}{39.09}}{\text{Al}/26.98} \tag{24.5}$$

Depending on whether analyses are reported as oxide or elemental concentrations, formula (24.1) or (24.2) is used, respectively. These calculations depend on Ca, K, and S analyses and on initial pH measurements. Concentrations of these three elements could, for example, be obtained in the field or at a mine site from an x-ray fluorescence analyzer. But the initial pH measurement must still be made in a laboratory, although the abrasion pH measurements reported by Stevens and Carron (1948) may prove to be an adequate substitute.

Once a functional relationship between alkali/aluminum ratios and initial pH has been established, an equation relating alkali/aluminum molar ratios to initial pH can be substituted for the initial pH measurements in the lithogeochemical NNP model. This means that all the data necessary for calculating the model can now be obtained directly from the whole-rock analyses. Depending on whether these analyses are reported as oxide or elemental concentrations, formula (24.3) or (24.4) is used, respectively. The molar alkali/aluminum ratio used in the modified lithogeochemical NNP models above and depending on whether major oxide or elemental analyses are used is calculated as shown in formula (24.5).

A comparison of modeled NNP values with measured NNP values (Figure 24.13) shows very good correlation. This demonstrates that the calculations above provide a reasonable approximation of the NNP values calculated by the BC Research method using S_{total} and SO_4 determinations and NP titration measurements.

Conclusions

The acid rock drainage buffering capacity of mine waste is governed by its bulk chemistry and its mineral assemblage. Samples of different rock types or of different alteration facies of the same rock type will have different ARD characteristics.

Conventional acid–base accounting tests can be used to predict short-term buffering but should be used with caution to model or predict long-term ARD buffering capacity. Conventional ABA reports the net results of acid–rock interaction tests but make no attempt to explain the geological, mineralogical, and geochemical factors that influence these results. The main problem with conventional ABA tests is that they are biased toward rapid ARD buffering by Ca- and Mg-bearing acid-soluble minerals in waste rocks.

It would be useful to conduct both short- and long-term tests to examine the modal mineralogy before, during, and after the buffering tests and then devise a model of the processes involved in ARD buffering.

Once the mineralogical parameters of ARD buffering processes have been recognized, lithogeochemical models using bulk chemistry might be devised.

Petrographic data must be examined together with lithogeochemical data to better understand acid–rock drainage parameters on a site-by-site basis. Theoretical (i.e., modeled) NNP will indicate buffering capacity over geological time, whereas laboratory-measured NNP indicates buffering over “run of mine life.”

Potential Uses

- The cost of analyzing major oxides, CO_2, and S_{total} is far lower than that for conducting NP tests for every sample.
- Because of transportable x-ray fluorescence equipment, analytical data from blast holes is now available for real-time determination of potential acid- and non-acid-generating waste material.
- The WPI measure of the weatherability of material should be used for construction purposes, blending, and kinetic test work.
- NP–time curves are a measure of buffering potential; use a graphical method to test for clays.

Summary

Rapid lithological and alteration classifications are important in acid rock drainage studies. Lithogeochemical data will help in understanding water quality data. Lithogeochemical methods should be used in any study for which blending or kinetic testing may be considered.

Reference and Suggested Reading

Cross, W., Iddings, J.P., Pirsson, L.V., and Washington, H.S., 1992. A quantitiative chemicomineralogical classification and nomenclature of igneous rocks. Journal of Geology, vol. 10, pp. 555–690.

Downing, B., and Madeisky, H.E., 1999. Lithogeochemical methods for acid rock drainage studies and prediction. Exploration and Mining Geology, vol. 6, no. 4, pp. 367–379.

Grant, W.H., 1969. Abrasion, pH: an index of chemical weathering. In: Clays and clay Minerals, Pergamon Press, London, vol. 17, pp. 151–155.

Stevens, R.E., and Carron, M.K., 1948. Simple field test for distinguishing minerals by abrasion pH. American Mineralogist, vol. 33, pp. 31–49.

25
Predicting Acid Rock Drainage based on Mineralogy and Petrology Studies

SHANNON SHAW AND BRUCE W. DOWNING

Mineralogical and petrological studies of the mineral products of oxidation of iron sulfide minerals pyrite (FeS_2) and pyrrhotite (FeS) in the presence of iron-oxidizing bacteria show the lithologic changes as sulfuric acid generation proceeds. A variety of methods and techniques are available to allow us to study these products of oxidation.

Introduction

The following chemical reactions relating to the oxidation of pyrite and the generation of sulfuric acid describe the oxidation of pyrite (FeS_2) to products that constitute the contaminants generically termed acid rock drainage (ARD), although similar equations may be written for the oxidation of pyrrhotite (FeS).

$$FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O = 15FeSO_4 + 8H_2SO_4 \quad (25.1)$$

$$FeS_2 + Fe_2(SO_4)_3 = 3FeSO_4 + 2S \quad (25.2)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \text{ bacteria} = 2Fe_2(SO_4)_3 + 2H_2O \quad (25.3)$$

$$2S + 3O_2 + 2H_2O \text{ bacteria} = 2H_2SO_4 \quad (25.4)$$

$$4FeS_2 + 15O_2 + 2H_2O = 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (25.5)$$

$$S^0 + 3Fe_2(SO_4)_3 + 4H_2O = 6FeSO_4 + 4H_2SO_4 \quad (25.6)$$

Neutralization of the acidic metal-rich solutions that can be generated by these chemical reactions may also occur as a result of the dissolution of neutralizing minerals (most important, carbonates) that come in contact with acidic solutions. These reactions must also be examined to fully understand the processes occurring and to be able to predict the chemistry of solutions resulting from a combination of oxidation and neutralization processes. Examples of these reactions include:

Calcite dissolution by sulfuric acid:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \quad (25.7)$$

Dolomite dissolution by sulfuric acid:

$$CaMg(CO_3)_2 + 2H_2SO_4 \rightarrow CaSO_4 + MgSO_4 + 2H_2O + CO_2 \quad (25.8)$$

Reactions of other gangue minerals may also contribute to the neutralization potential of the system under specific pH conditions (Ritchie, 1994):

Muscovite dissolution:

$$KAl_2[AlSi_3O_{10}](OH)_{2(s)} + H^+ + \tfrac{3}{2}H_2O \rightarrow K^+ + \tfrac{3}{2}Al_2Si_2O_5(OH)_{4(s)} \quad (25.9)$$

Biotite dissolution:

$$KMg_{1.5}Fe_{1.5}AlSi_3O_{10}(OH)_{2(s)} + 7H^+ + \tfrac{1}{2}H_2O \rightarrow K^+ + \tfrac{3}{2}Mg^{2+} + \tfrac{3}{2}Fe^{2+} + H_4SiO_4^0 + \tfrac{1}{2}Al_2Si_2O_5(OH)_{4(s)} \quad (25.10)$$

Albite dissolution:

$$NaAlSi_3O_{8(s)} + H^+ + \tfrac{9}{2}H_2O \rightarrow Na^+ + 2H_4SiO_4^0 + \tfrac{1}{2}Al_2Si_2O_5(OH)_{4(s)} \quad (25.11)$$

Anorthite dissolution:

$$CaAl_2Si_2O_{8(s)} + 2H^+ + H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_{4(s)} \quad (25.12)$$

K-feldspar dissolution:

$$KAlSi_3O_{8(s)} + H^+ + \tfrac{9}{2}H_2O \rightarrow K^+ + 2H_4SiO_4^0 + \tfrac{1}{2}Al_2Si_2O_5(OH)_{4(s)} \quad (25.13)$$

Iron oxyhydroxide dissolution:

$$Fe(OH)_{3(s)} + 3H^+ \rightarrow Fe^{3+} + 3H_2O \quad (25.14)$$

When studying these reactions and processes, mineralogy is the key factor. In many instances, both ARD reactions are studied to assess or predict future water quality, and mineralogy can provide key insights, even though detailed mineralogy is often time consuming, expensive, and specialized.

Methods and Techniques

Petrographical or mineralogical examination of samples in ARD predictive work is usually conducted by transmitted- and reflected-light microscopy and by various x-ray diffraction (XRD) techniques. Although electron probe microanalysis, scanning electron microscopy, and other more specialized techniques are employed, their use is generally confined to sulfide minerals where compositional abnormalities affect ARD test work interpretation. Such techniques are particularly useful for determination of the chemical composition of sulfide oxidation products, such as rims, inclusions, and amorphous (noncrystalline) species.

Transmitted-light microscopy utilizes thin (30-μm) sections of samples, and reflected-light microscopy utilizes polished mounted samples. Current practice combines the two sample preparation procedures to produce polished thin sections, so that the two techniques can be used on the same sample. McCrone et al. (1979) describe the techniques of thin- and polished-section microscopy in detail. Samples may be prepared from whole rock in the form of a drill core, or from fragmented material such as humidity cell feed and residue samples, or from tailings.

Transmitted-light microscopy is used to examine those minerals that transmit light in thin section, and these include most of the gangue or nonmetallic minerals that may have neutralizing capability. Reflected-light microscopy is used to examine those minerals that do not transmit light in thin section but reflect light to varying degrees when polished. Such minerals include metallic sulfides that may oxidize to generate acid. Both types of microscopy are used (often with supplementary techniques such as selective staining or etching) to identify individual mineral grains, to determine mineral grain size and size distribution, and to identify mineral grain spatial interrelationships.

Reaction products of sulfide oxidation (rimming of grains) are readily observed, as are many other characteristics of mineral grains (such as inclusions) not readily seen by other investigative techniques. These capabilities of microscopic examination are extremely useful in ARD studies of both tailings and waste rock. The ultimate size limitation of these methods is the wavelength of the light used and the optical arrangement of the microscope, but it is typically about 1 μm in grain size. Consequently, samples containing significant quantities of clay minerals (<2 μm) present identification problems for the microscopist.

It is usually possible to determine the frequency of occurrence of individual minerals within a sample by the examination of a number of fields of view. Quantitative mineralogical analysis by this method is termed *modal analysis*. For some well-defined unaltered rock types it has been possible to calculate a modal analysis (or quantitative mineralogical analysis) from elemental oxide analyses of whole-rock samples using mathematical techniques. Such calculations, known as CIPW from the initials of their original developers (Cross et al., 1902), can be undertaken by computer programs such as NewPet for DOS (Clarke, 1993). However, for the rock types typically associated with significant sulfide mineralization, CIPW calculations have not yet been shown to have general applicability (Lawrence and Sheske, 1997; Paktunc, 1998c) because they were developed for unaltered magmas and cannot be applied to sedimentary or metamorphic rocks or to altered igneous rocks. This is most unfortunate, since whole-rock elemental oxide analysis is generally less expensive than microscopic analysis and does not require the considerable skill of a mineral microscopist. Paktunc (1998b) developed a computer program called MODAN that may be used to determine modal mineralogy from whole-rock elemental oxide analysis and a knowledge of the mineral species present in a sample. Paktunc (1998a) has also discussed the use of MODAN in the conjunction of mineral reactivity data to estimate the neutralizing potential of samples containing neutralizing silicates in addition to carbonates.

Low-power stereoscopic microscopy is also a useful tool, particularly in the examination of tailings and other relatively fine, fragmented samples. This technique is valuable in the determination of the degree of sulfide mineral liberation and may also be used as an aid in sulfide mineral identification. The identification of mineral grains has been well covered by Jones and Fleming (1965). It is usually preferable to examine screen-size fractions when using low-power stereoscopic microscopy, and it is also helpful to remove the bulk of the gangue mineral particles using one or more heavy liquid procedures at a relative density of 2.8 to 2.9 (Mills, 1978, 1985).

Some workers (Jambor and Blowes, 1998) obtain an x-ray diffractogram for each sample examined by transmitted- and reflected-light microscopy and compare the mineral identification data obtained from the

two procedures for corroboration. This approach is highly recommended.

Individual mineral grains greater than about 100 μm may be positively identified by x-ray diffraction (XRD) using the x-ray film method using Debye–Scherrer or Gandolfi cameras or modern microdiffractometry instruments (Jambor and Blowes, 1998). These XRD methods all give qualitative data on mineral identity.

Examples

It is own intention here to act as an introduction to the mineralogical and petrological basics associated with ARD in an effort to emphasize the importance of mineralogical characterization in ARD studies and prediction. One of the major criticisms of petrological characterization of minerals is that it is largely nonquantitative or semiquantitative. In an effort to quantify sulfide oxidation, Blowes and Jambor (1990) have developed a sulfide alteration index (SAI) tailored to the oxidation of mine wastes. Although it is objective, it serves to put into relative terms the degree of oxidation occurring or having occurred at one site and give an indication of the progression and remaining oxidation of a particular waste, as it is easily adapted to specific-site mineralogy. The index (developed initially for the Waite Amulet Tailings, Quebec) is reproduced in Table 25.1.

Table 25.1 Index Scale for the Degree of Alteration of Sulfides

Numerical Scale	Degree of Alteration of Sulfides
10	Pyrrhotite and pyrite obliterated; only traces of sulfide; typically, chalcopyrite is present.
9	Similar to 10, but with a few scattered remnant grains of pyrite.
8–7	First appearance of trace amounts of pyrrhotite (at scale 8); at scale 7 the vestiges of strongly altered pyrrhotite increase in abundance or degree of preservation.
6–2	At scale 6 the pyrrhotite grains have broad alteration rims, but the cores of numerous grains are preserved; gradation to scale 2 is marked by the appearance of narrower alteration rims and a predominance of unaltered grains.
1–0	Only a few grains of pyrrhotite are weakly altered along rims and fractures; >95% of the grains have sharp, fresh margins.

A second criticism of petrological characterization of minerals is that it is relatively abstruse to the majority of people studying in this field. Figures 25.1 through 25.9 are photomicrographs, and their corresponding descriptions and interpretations have been included as examples of sulfide oxidation and dissolution of neutralizing minerals from various sites throughout North America. In Figure 25.1, alteration is proceeding as preferential replacement along the {0001} crystallographic parting plane. The alteration (secondary) mineral phase is predominantly an iron oxyhydroxide. Figure 25.2 demonstrates the different alteration rates between pyrrhotite and pyrite. Alteration of pyrrhotite in this case is occurring both around the grain periphery and along the parting plane. In Figure 25.3, both the pyrrhotite and pentlandite exhibit alteration to iron oxyhydroxides at approximately equal rates of oxidation; however, the alteration textures are significantly different. Pyrrhotite shows predominant alteration along the grain's parting plane, whereas pentlandite alteration is seemingly nonpreferential, primarily along fractures in the grain.

Figure 25.4 suggests that significant sulfide alteration has occurred, producing iron and sulfates that have

re-precipitated out of solution as iron oxyhydroxides (orangey red) and gypsum (white). These cementing phases probably serve to slow further oxygen penetration and therefore sulfide oxidation. Figure 25.5 depicts the complete pseudomorphic replacement of pyrrhotite. In reflected light the alteration product looks relatively homogeneous; under crossed Nicols, however, it is clear that it is a multiphased and progressive replacement. This grain was examined in further detail as described below.

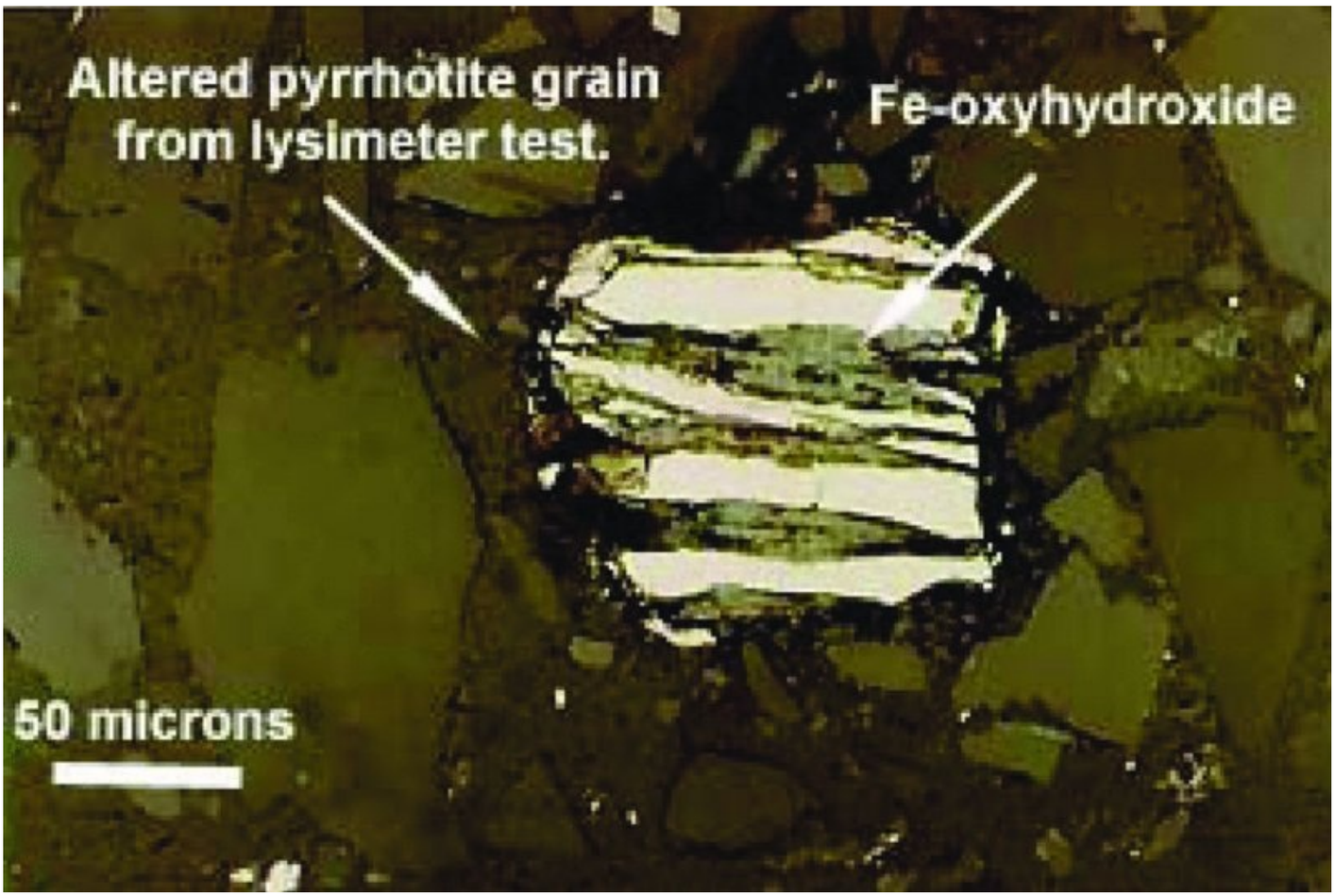


Figure 25.1 Reflected-light photomicrograph of altered pyrrhotite grain.

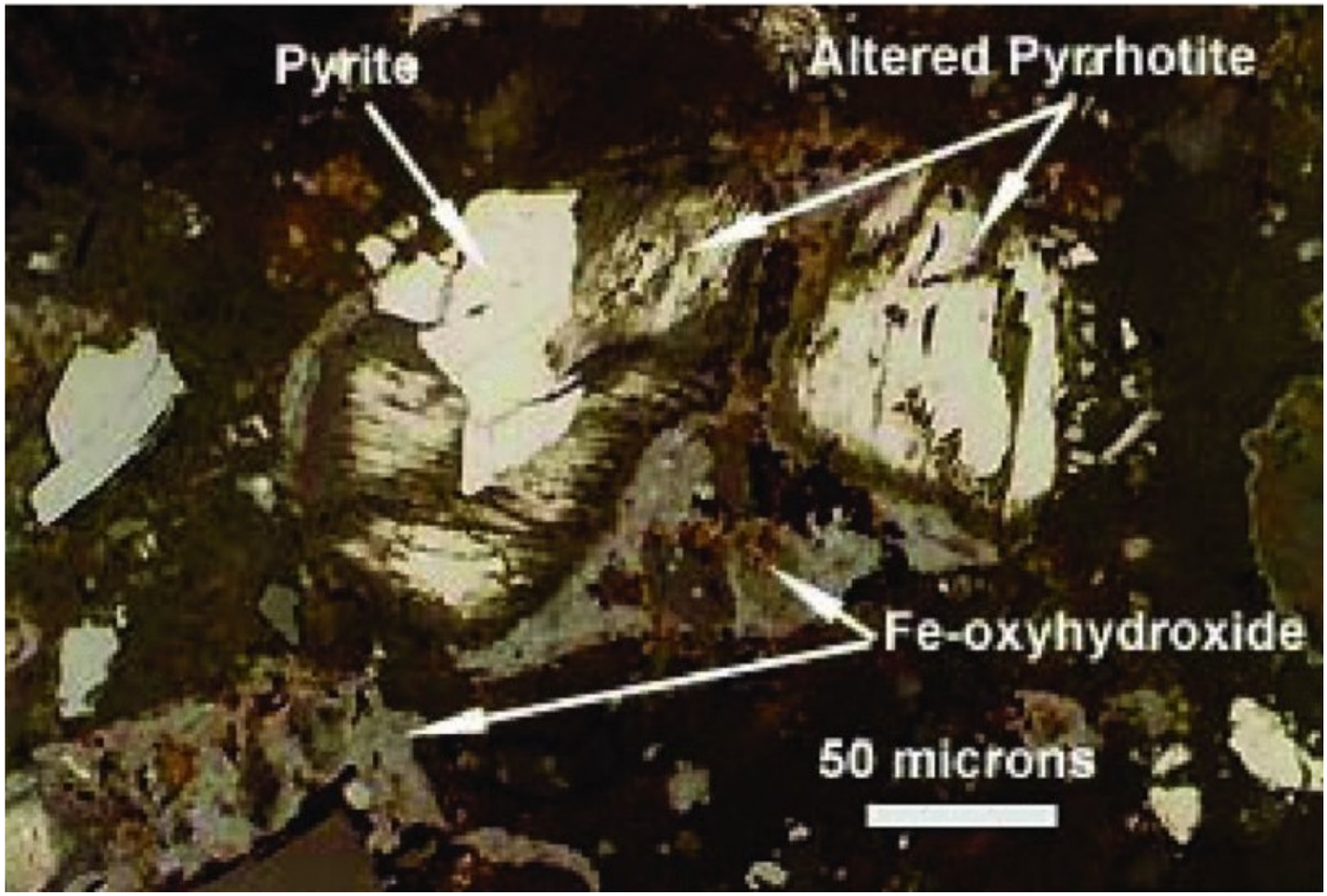


Figure 25.2 Reflected-light photomicrograph of altered pyrrhotite and unaltered pyrite grains.

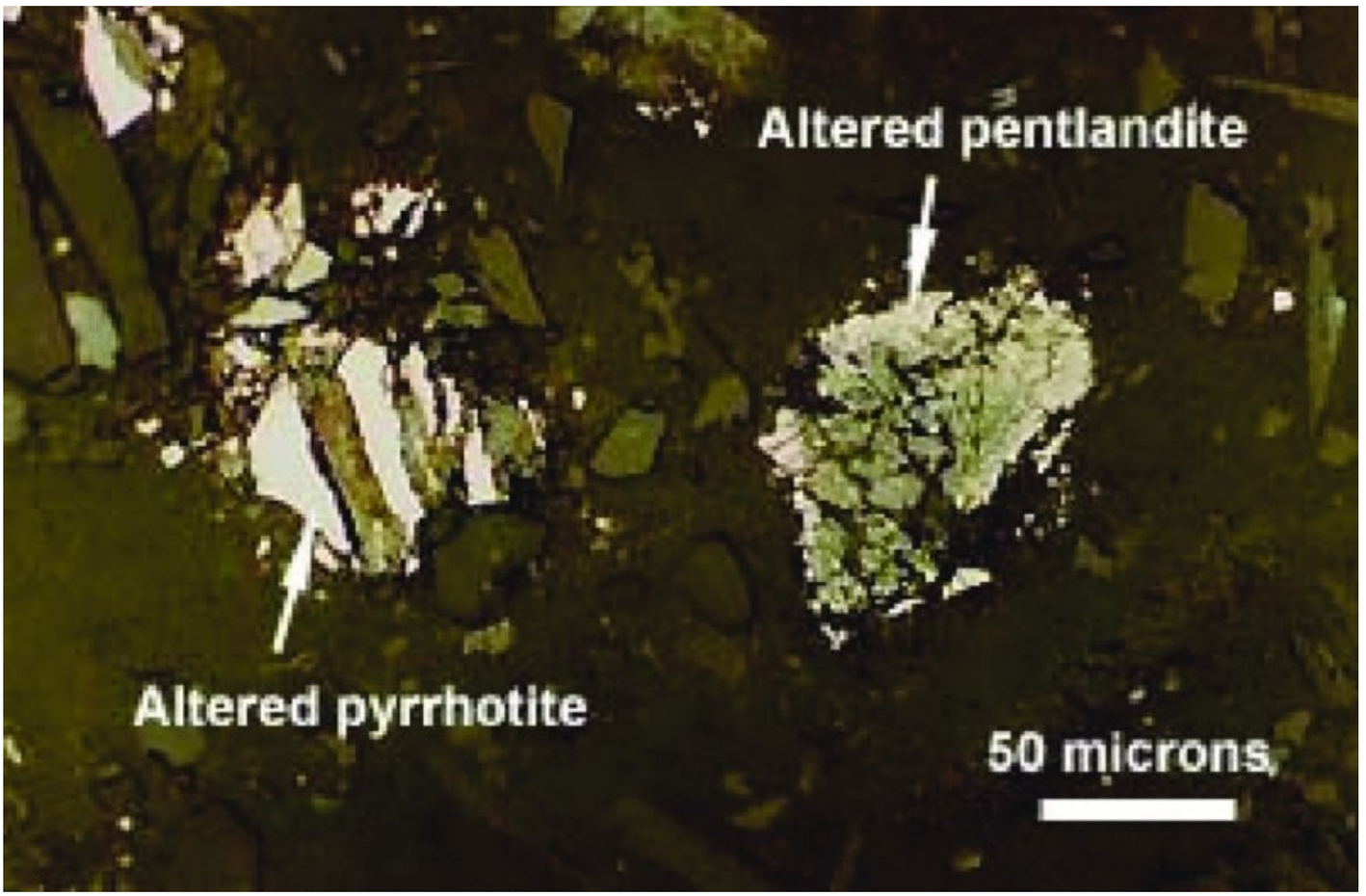


Figure 25.3 Reflected-light photomicrograph of altered pyrrhotite and pentlandite grains.

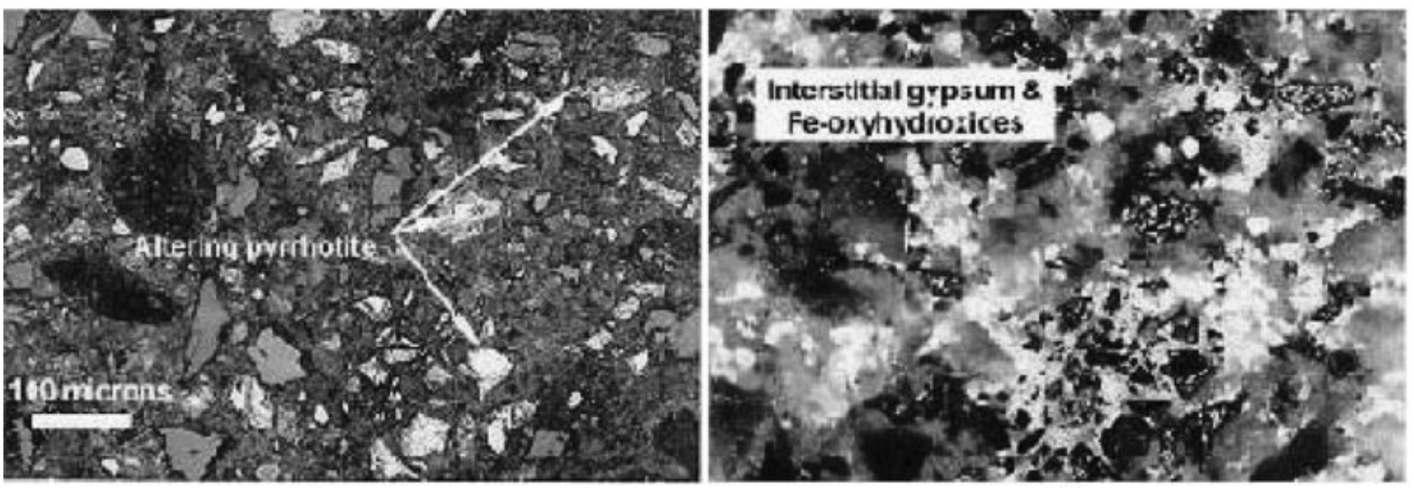


Figure 25.4 Photomicrographs of altering pyrrhotite grains and associated primary minerals “cemented” by secondary gypsum and iron oxyhydroxides (a) in reflected light and (b) under crossed Nicols.

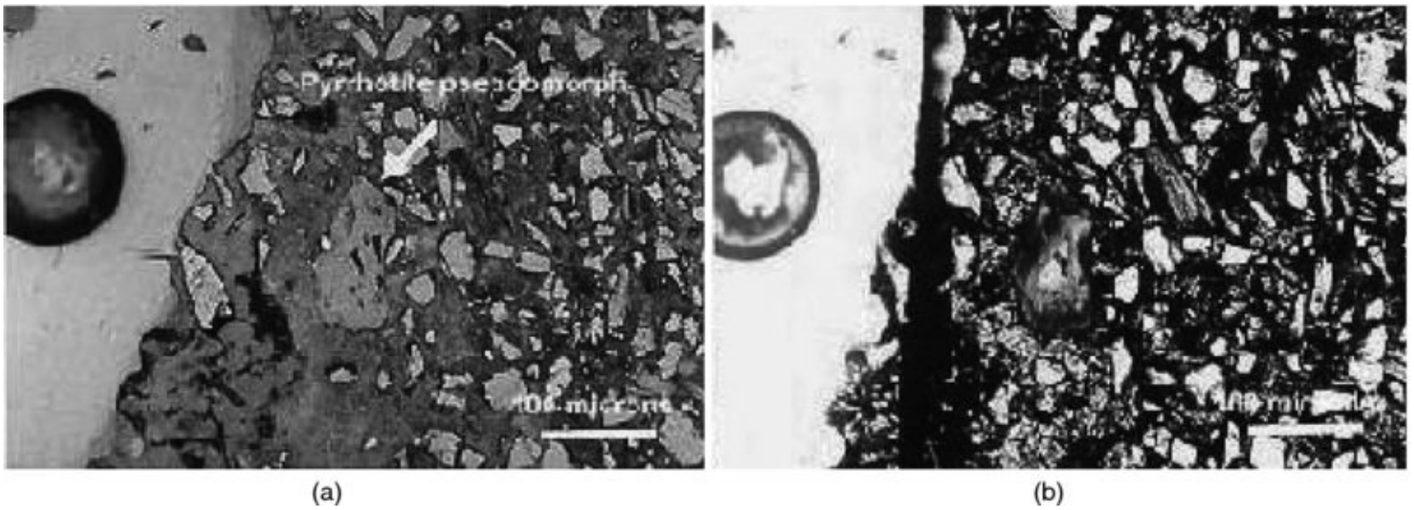


Figure 25.5 Photomicrographs of pyrrhotite pseudomorph (a) in reflected light and (b) under crossed Nicols.

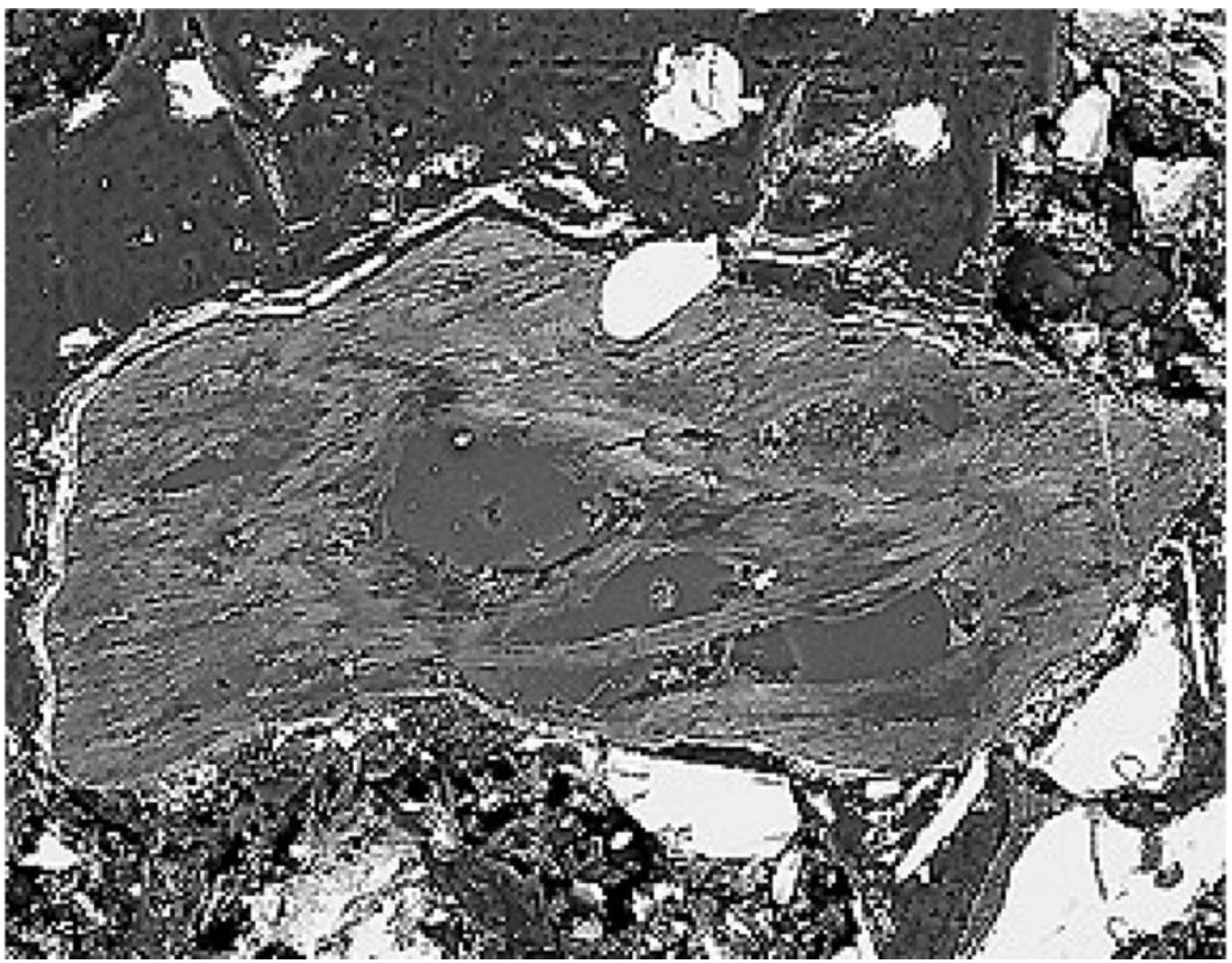


Figure 25.6 Backscattered electron image of pyrrhotite pseudomorph (field of view, 300 μm).

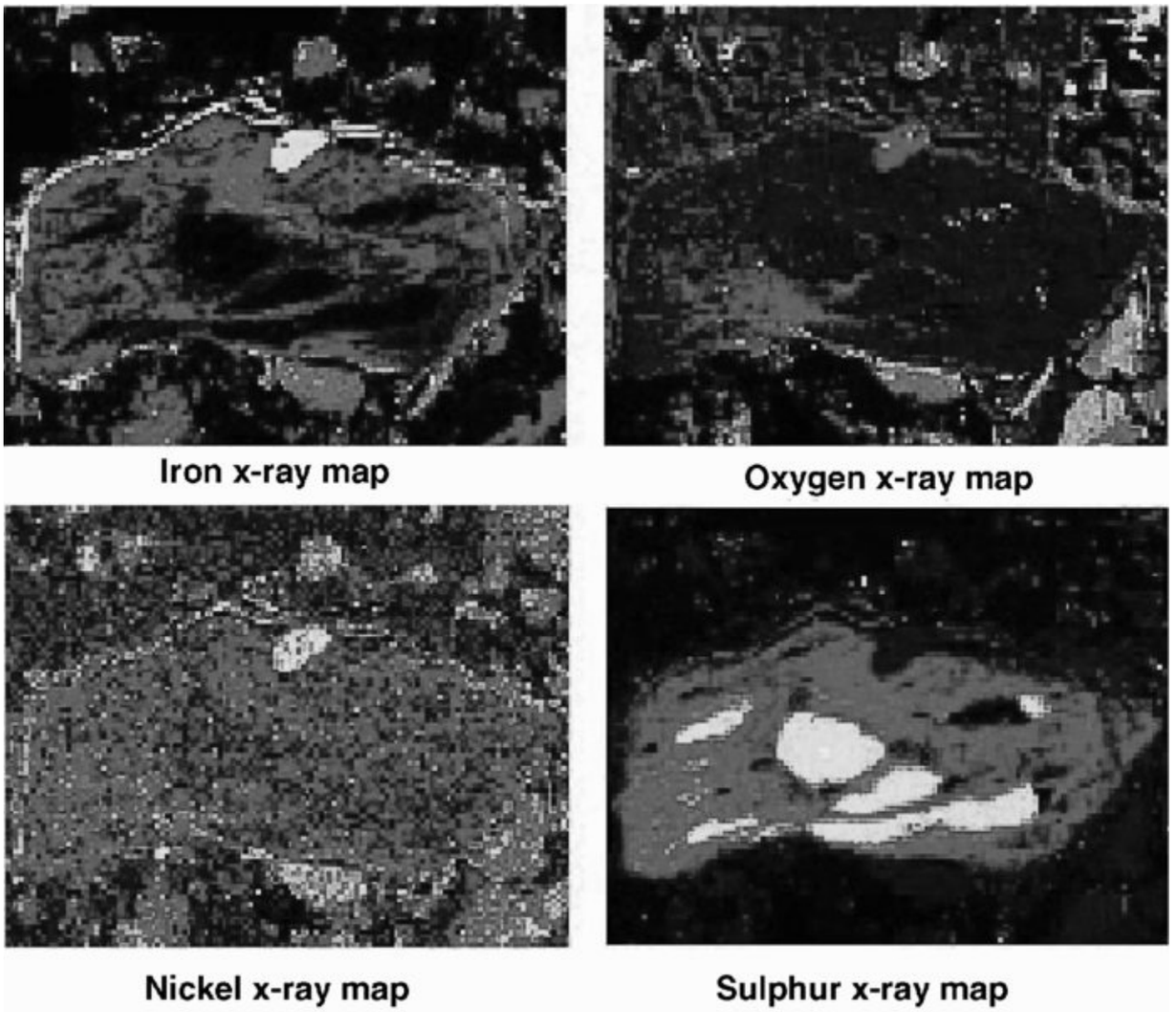


Figure 25.7 Element x-ray maps of the same pseudomorph (field of view, 300 μm).

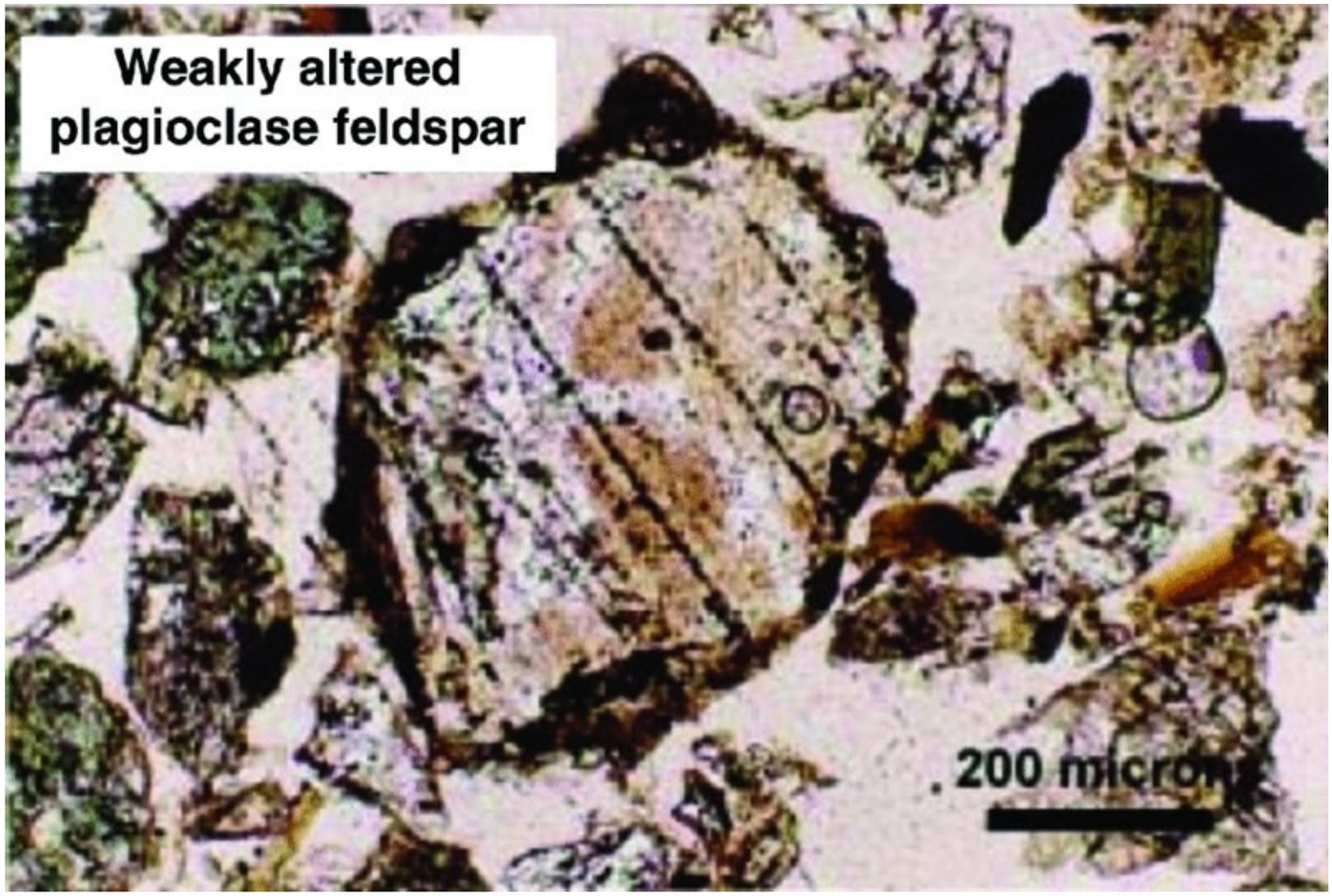


Figure 25.8 Transmitted-light photomicrograph of weakly altered plagioclase feldspar.

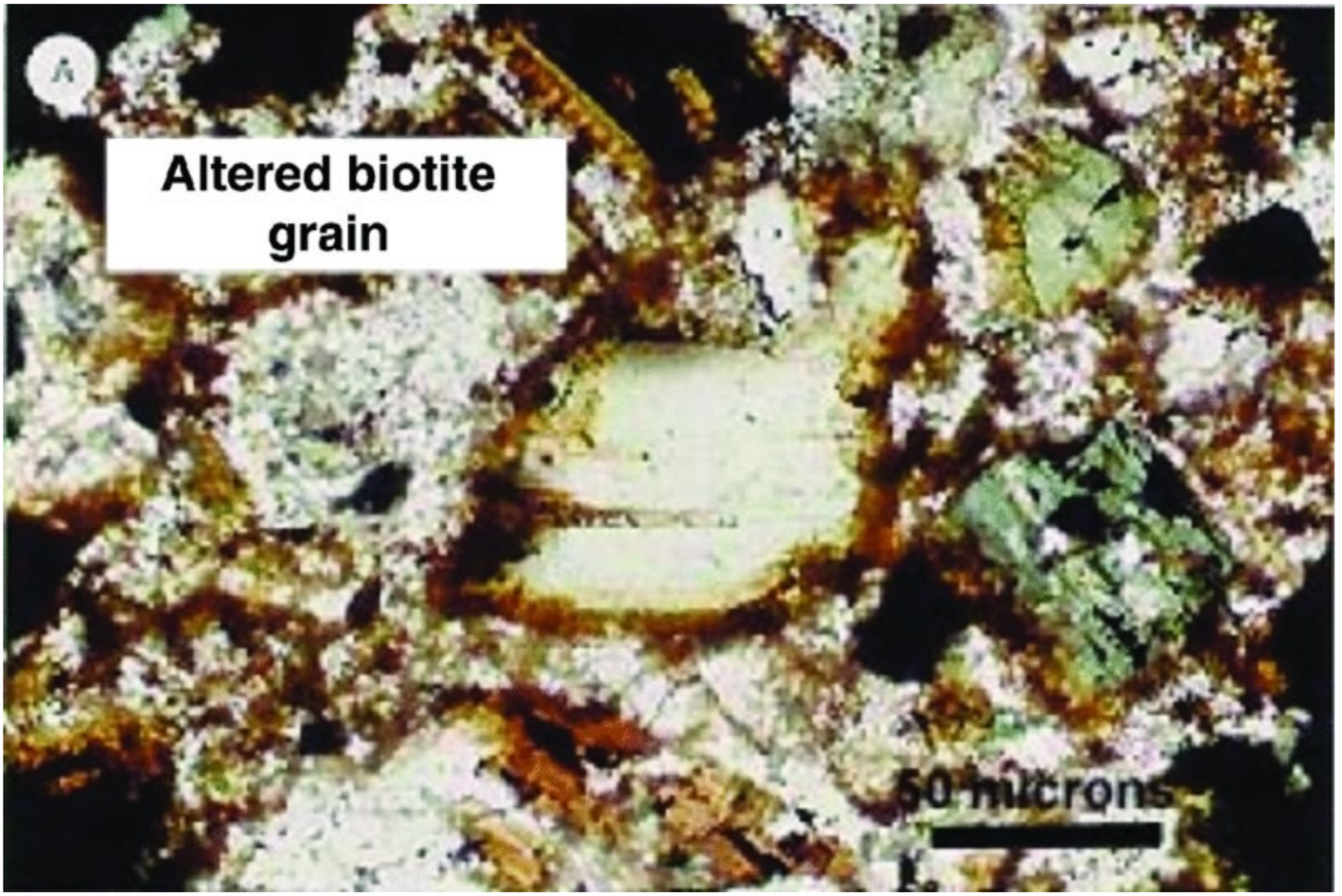


Figure 25.9 Transmitted-light photomicrograph of altered biotite grain.

Many of the mineralogical processes of interest and importance that control the acid generation/metal leaching character of mine waste occur on a small scale (micrometer level), in particular for tailings. For this reason, use of the scanning electron microscope (SEM) can greatly aid in the understanding and therefore interpretation of these mineralogical controls. For example, the pyrrhotite pseudomorph shown in Figure 25.5(turned 90°) was examined under an SEM using both backscattered electron imagery (BSE) and elemental x-ray maps, as shown below.

The BSE image (Figure 25.6) allows for detailed examination of the texture of this grain. The pseudomorphic replacement occurred along a preferred orientation, probably along the {0001} crystallographic parting plane. It also appears that portions of the pseudomorph are more crystalline than others. The x-ray maps (Figure 25.7) allow for nondestructive, semiquantitative analysis of the chemistry of alteration products.

Although documenting a snapshot in time, these mineralogical tools illustrate clearly that alteration of sulfides is a progressive process with complex mineralogical changes occurring throughout and various intermediate phases dominating different stages. The grain shown would be classified on the SAI in Table 25.1 as a 9 or 10, depending on the alteration of other sulfides in the sample. If this grain were typical of an entire site, it might suggest that the rate of oxidation, and therefore acid generation, would be slowing. This conclusion could affect the selection of particular control technologies or closure requirements. For example, the selection of a complex tailings cover to prevent oxygen infiltration as a means of controlling sulfide oxidation at a site where the sulfides were typical of the example above may not be appropriate.

Other predictive tools that are commonly used include acid–base accounting (ABA) tests and other static

and kinetic laboratory procedures. Interpretation of these results is critical, and as proven more than once, very site-specific. One of the issues most difficult to interpret is the neutralization potential (NP) of the ABA test. Carbonates play a dominant role in acid neutralization, but other minerals, depending on pH conditions, can contribute to NP. Plagioclase feldspar and biotite are two such minerals (Figures 25.8 and 25.9).

Weak alteration of the plagioclase feldspar, known as *saussuritization* is shown in Figure 25.8. The grain is also rimmed by fine-grained iron oxyhydroxide precipitating from solution. Significant alteration in the biotite grain shown in Figure 25.9 is evidenced by the loss in color and pleochroism. Electron probe microanalyses of similar altered biotite grains showed a depletion in K, Fe, and Mg, indicating alteration to vermiculite. Similar results were reported by Jambor (1994). This grain, as was seen with the plagioclase in Figure 25.8. is coated with a secondary phase, probably an iron oxyhydroxide.

The identification of secondary alteration products also plays an important role in the prediction of pore water quality. Geochemical equilibrium speciation models such as MINTEQA2 (Allison et al., 1991) are frequently used for these predictions. Pore water chemistry is dependent on the solubility constraints of the minerals through which the pore water migrates. Therefore, minerals identified during mineralogical characterization, in particular the secondary alteration products and carbonates, can be used in geochemical models as constraints and controls on the pore water chemistry predicted.

References and Suggested Reading

Allison, J.D., Brown, D.S., and Novo-Grada, K.J., 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems, Version 3.0. EPA/600/3-91/021. U.S. EPA, Office of Research and Development, Athens, GA.

Blowes, D.W., and Jambor, J.L., 1990. The pore-water geochemistry and the mineralogy of the vadose zone of sulfide tailings, Waite Amulet, Quebec, Canada. Applied Geochemistry, vol. 5, pp. 327–346.

Clarke, D., 1993. NewPet for DOS. Department of Earth Sciences, Memorial University of Newfoundland, St. John's, NF, Canada.

Cross, W., Iddings, J.P., Pirsson, L.V., and Washington, H.S., 1902. A quantitative chemicomineralogical classification and nomenclature of igneous rocks. Journal of Geology, vol. 10, pp. 555–690.

Jambor, J.L. 1994. Mineralogy of sulfide-rich tailings and their oxidation products. In: Environmental Geochemistry of Sulfide Mine-Wastes. Mineralogical Association of Canada Short Course, vol. 22, pp. 59–102.

Jambor, J.L., and Blowes, D.W., 1998. Theory and application of mineralogy in environmental studies of sulfide-bearing mine wastes. In: Modern Approaches to Ore and Environmental Mineralogy, L.J. Cabri and D.J. Vaughan, eds., Mineralogical Association of Canada Short Course, vol. 27, pp. 367–402.

Jones, M.P., and Fleming, M.G., 1965. Identification of Mineral Grains. Elsevier, London, 102 pp.

Kwong, Y.T.J., and Ferguson, K.D., 1997. Mineralogical changes during NP determinations and their implications. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, pp. 435–447.

Lawrence, R.W., and Sheske, M., 1997. A method to calculate the neutralization potential of mining

wastes. Environmental Geology, vol. 32, pp. 100–106.

McCrone, W.C., McCrone, L.B., and Delly, J.G., 1979. Polarized Light Microscopy. Ann Arbor Science, Ann Arbor, MI, 251 pp.

Mills, C., 1978. Mineralogy and Heavy Liquid Analysis in Gravity Separation. Short Course on Gravity Concentration Technology. University of Nevada, Reno, NV, 25 pp.

Mills, C., 1985. Specific gravity fractionation and testing with heavy liquids. In: SME Mineral Processing Handbook. American Institute of Mining, Metallurgical and Petroleum Engineers, New York, vol. 30, pp. 44–52.

Paktunc, A.D., 1998a. Characterization of mine wastes for the prediction of acid mine drainage. In: Environmental Impacts of Mining Activities: Emphasis on Mitigation and Remedial Measures, J.M. Azcue, ed., Springer-Verlag, Berlin.

Paktunc, A.D., 1998b. MODAN: an interactive computer program for estimating mineral quantities based on bulk composition. Computers and Geosciences, vol. 24, no. 5, pp. 425–431.

Paktunc, A.D., 1998c. Discussion of “A Method to Calculate the Neutralization Potential of Mining Wastes,” R.W. Lawrence and M. Sheske. Environmental Geology, vol. 32, pp. 100–106.

Ritchie, A.I.M., 1994. The waste-rock environment. In: Environmental Geochemistry of Sulfide Mine-Wastes. Mineralogical Association of Canada Shortcourse Handbook, J.L. Jambor and D.W. Blowes, eds., vol. 22, pp. 133–161.

26
Management and Analysis of Acid Drainage Data

BRUCE W. DOWNING

The management and analysis of data derived from acid rock drainage (ARD) studies is essential for predictions, conclusions, and recommendations. The precursor to data management and analysis is the sampling program (Price 1997, 1998). Sampling is the single most important aspect of a good survey, for without good sampling, analytical results may not be valid and hence correct interpretations will be difficult to achieve. Sampling with respect to acid rock drainage material is discussed by Downing and Shaw (2000), and quality assurance and quality control is discussed by Downing and Mills (1998b). The purpose of this chapter is to focus on concepts and methods involved in data management and analysis. This then becomes part of the environmental management plan for the project site (Bellefontaine, 2006).

Introduction

The collection of data begins in the field with qualified people who must be involved from the initial data gathering through to the laboratory test work, interpretations, and conclusions. The first goal of the ARD practitioner is to characterize the material and determine its potential for generating acid and potential metal-leaching capacity (of the material) with such categories as:

- Acid generation (AG)
- Potential acid generation (PAG)
- Potential acid consumption (PAC)
- Acid consumption (AC)

These groups are all predicated on a single threshold number, upon which many dollars must be spent either treating the material or disposing of it in a proper manner. Poor sampling, poor laboratory analysis, and poor data analysis can make the difference in either spending or saving millions of dollars.

Data

ARD data are derived from several sources.

1. *Field data.* Field data consist of observations and collection parameters, collectively called *observational data*, collected at the site being examined.
2. *Analytical data.* Analytical data generally consist of acid–base accounting (ABA) parameters (neutralization potential, total sulfide, sulfate sulfur, carbon dioxide), trace element, whole rock (major oxides), and water quality analyses. Major components of the investigative process are both the method of analysis and the type of sample digestion.
3. *Site test data.* The field laboratory site test work involves constructing waste rock test pads on site to monitor leachate from the various types of waste material under field conditions.
4. *Laboratory site data*. Laboratory site data consist of kinetic and humidity cell testators. These types

of tests can in many ways be classified as producing experimental data obtained under controlled conditions. Laboratory tests are discussed by Shaw and Mills (1998).

5. *Mineralogical data*. Mineralogical data consist of thin-section and x-ray diffraction techniques to determine the modal mineralogy (Shaw and Mills, 1995). The contribution of specific minerals to the neutralization potential is important in understanding the various static (and kinetic) test results (Jambor et al., 1998b).

Data Variability

There are four types of variability in geological and ARD data (Koch and Link, 1980):

- *Natural variability*: variability inherent in the geological material being sampled
- *Sampling variability*: variability produced by the physical sampling process
- *Preparation variability*: variability introduced when preparing material for chemical analysis by crushing, pulverizing, splitting and sub-sampling.
- *Analytical variability*: variability introduced by the chemical or physical determination of substances in the geological material

Data Management

What constitutes a good database, and how reliable is it? Data integrity is a constant concern. Construction of a valid database begins with good sample collection. Appropriate sample collection, preparation, analytical procedures, and standards must be maintained throughout project life. Errors can be generated throughout the entire scenario of a project, from data collection, preparation, analysis, input, transfer, and merging through to reporting.

How to eliminate or minimize errors is not the question during data analysis, but how to recognize, correct, and report them are of major importance. Check sampling and validation of a database should be carried out even though it is time consuming to the point of being boring. Error recognition can be achieved through periodic printouts and plots and/or by a complete database dump followed by manual editing. This also provides a quick data reference. One should generate ways of cross-checking the data through the use of plots or mathematical manipulation, querying all results and basic statistics. There is always an element of luck in spotting errors before final reporting. Errors always seem to crop up at the most inappropriate times. In reserve estimation, there are numerous mathematical manipulations where incorrect data can generate incorrect results. An effective method of error reduction is having the project people involved directly in the data analysis and reporting since they can best identify incorrect results generated through data processing.

A valid database is still prone to problems when it is subdivided into sections for analysis using similar or different software, manipulations and calculations performed, and data dumped back into the original database. Retaining current database versions is very important, as well as documenting the entire database. A central, currently correct database must be maintained securely, together with routine backups and off-site storage of databases. The end product should always be subject to the question: How defensible are my data?

Data Analysis

ARD data do not generally form a normal distribution but often more closely resemble a lognormal

distribution, and statistical assumptions may fail to describe the real data behavior. Evaluation of the data can range from simple plots and statistics to more rigorous statistical analysis, which at this stage would require the services of a qualified statistician. For most ARD applications, the former is the standard; very few studies have ever used the latter, as is evident from the lack of published papers or presentations at ARD conferences. The analytical data are essentially geochemical data, the evaluation of which is the focus of numerous papers published in geochemical journals (Garrett et al., 1998a; Kurzl, 2000). Comparisons of ARD predictions with historical data and case histories can be advantageous to the practitioner (Morin, 1997; Price, 2005).

Whatever methods are used by the ARD practitioner, they should be easily understood, visual (graphical presentations), and easy to apply. Several computer statistical programs deal with rigorous statistical analysis of the data. Computer spreadsheet programs generally contain features that can be used for a much less rigorous approach to the statistical analysis of the data. These programs also contain plotting features that are necessary for the visual interpretation and presentation of the data. When utilizing multivariate statistics, one must be reasonably competent or employ the services of a qualified statistician.

Data Plot Analysis

Some useful plots that can aid in the interpretation of data are discussed below.

Scattergrams

Scattergrams (x–y plots) are very useful in viewing data to detect linear correlations. If there appears to be a relationship, a regression equation and correlation coefficient can be calculated to determine the degree of linearity between the two variables. Examples of scattergrams follow.

- *MPA versus* S_{total} *plot* (Figure 26.1. This type of plot shows the distribution of sulfate in a sample. For samples with no sulfate, there will be a straight line, as MPA = S% total; if a sample does contain sulfate, it will plot below the line. Sulfur speciation is an integral part of this analysis, as discussed by Day et al. (1997).
- *Neutralization plots*. These plots are useful for observing the major contributors to the neutralization potential (or buffering minerals).
    1. *CO_2 versus NP* (Figure 26.2). This type of plot indicates the importance and distribution of carbonate for neutralization. If there is a direct (positive) correlation, the assumption that NP is attributable to carbonate is correct.
    2. *Test for surrogate elements* (*Ca vs. NP*; Figure 26.3). If the evaluation of CO_2 versus NP is positive, calcium-bearing carbonate must be examined using a Ca versus NP plot. If again if there is a positive correlation, one can assume that Ca could be used as a surrogate for a neutralization potential (Downing and Giroux, 1995; Day, 1992; Kwong, 1970). Other surrogate element tests are Mg versus NP and Ca + Mg versus NP.
    3. *NP versus MPA* (Figure 26.4). This type of plot shows the spatial distribution of neutralization and acidity. This plot is useful for presenting the acid rock–generating potential of samples analyzed.
- *Carbonate speciation*. This type of analysis is very important in determining the main carbonate species, which has a major implication for the neutralization potential. This can be done using various

stains for calcite and dolomite or analytical techniques (Day, 1992).

- *Fe versus Al* (Figure 26.5). This type of plot is based on work by Bladh (2000) which shows the propensity of sulfate minerals (goethite, jarosite, alunite) to form from the bulk chemistry of a sample. This is useful in predicting which samples will form these minerals when oxidized and weathered.
- *Trace element plots*. Trace element plots should be used to show the distribution of trace elements that occur with varying lithologies, both ore- and non-ore-grade material, and spatially within a deposit. It should be noted that it is not sufficient to calculate an average or median value for each trace element, due to the potential variability within a deposit. Methods of trace element analysis are discussed by Downing and Mills (1998a).
- *Three-dimensional plots*. This type of plot can be devised using bubble plots, three-dimensional plot visualization, or ternary diagrams, all of which are available in various software packages. An example of using bubble plot analysis is presented in Figure 26.6. Figure 26.6a shows rock types using the TiO_2 versus Zr classification; Figure 26.6b shows the same rock type classification but with a bubble indicating the NP/MPA ratio, indicative of which rock type has a better neutralization potential. These types of plots are good for examining more than three variables.

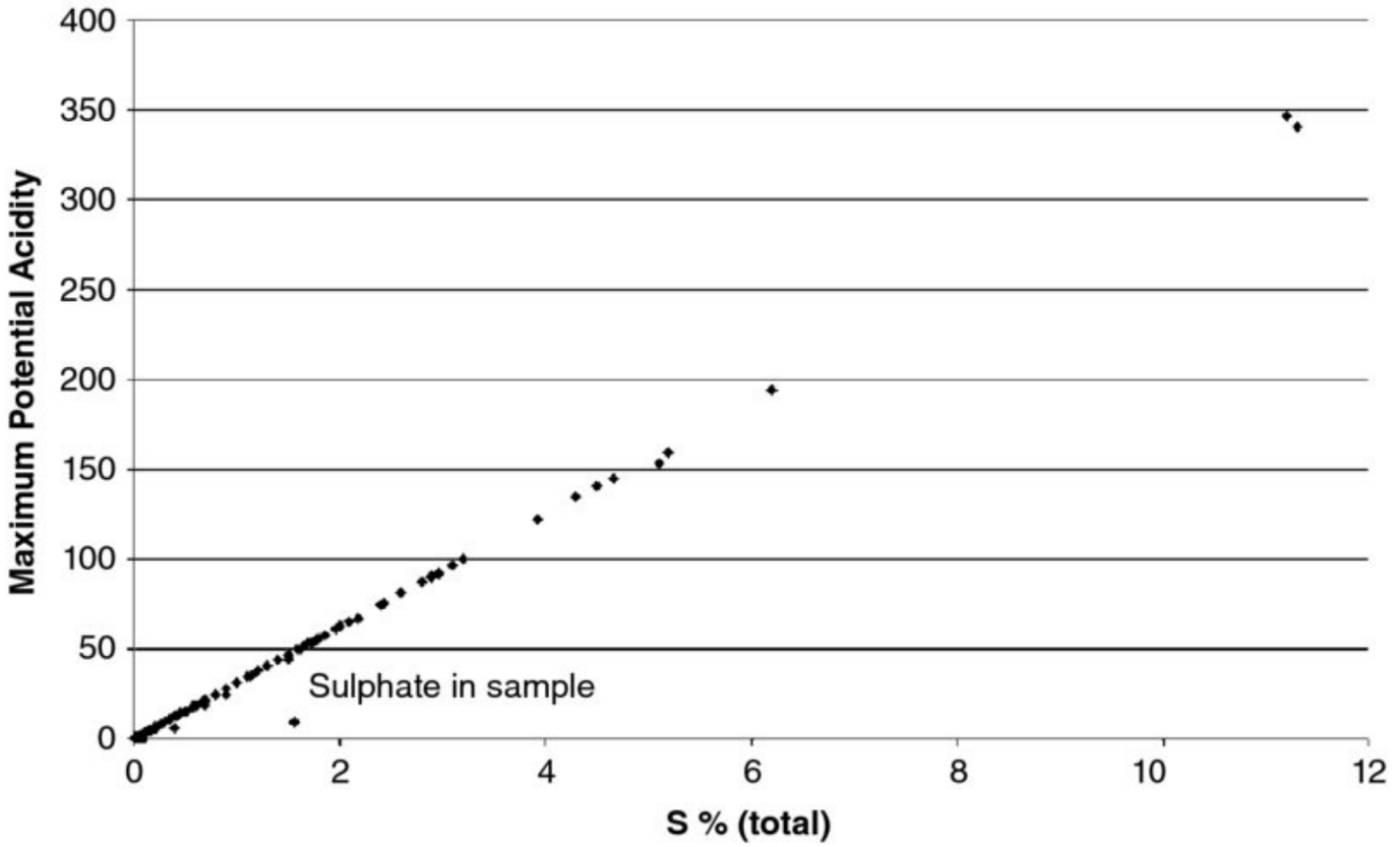


Figure 26.1 Plot of maximum potential acidity versus total sulfur.

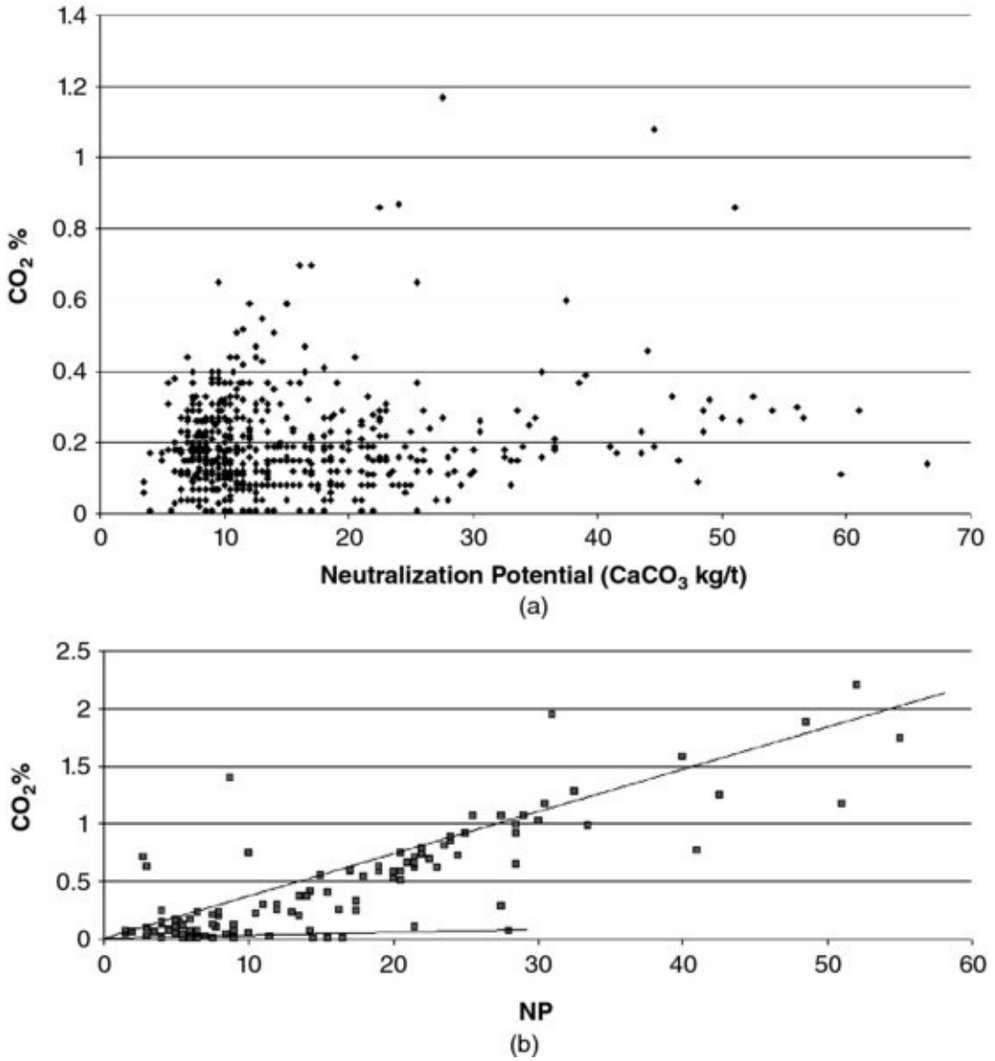


Figure 26.2 (a) NP not related to carbonate, and carbonate occurs in trace amounts; (b) CO_2 versus NP (distribution of carbonate for neutralization; note two rock types). NP is related to carbonate in most samples but probably related to a specific rock unit.

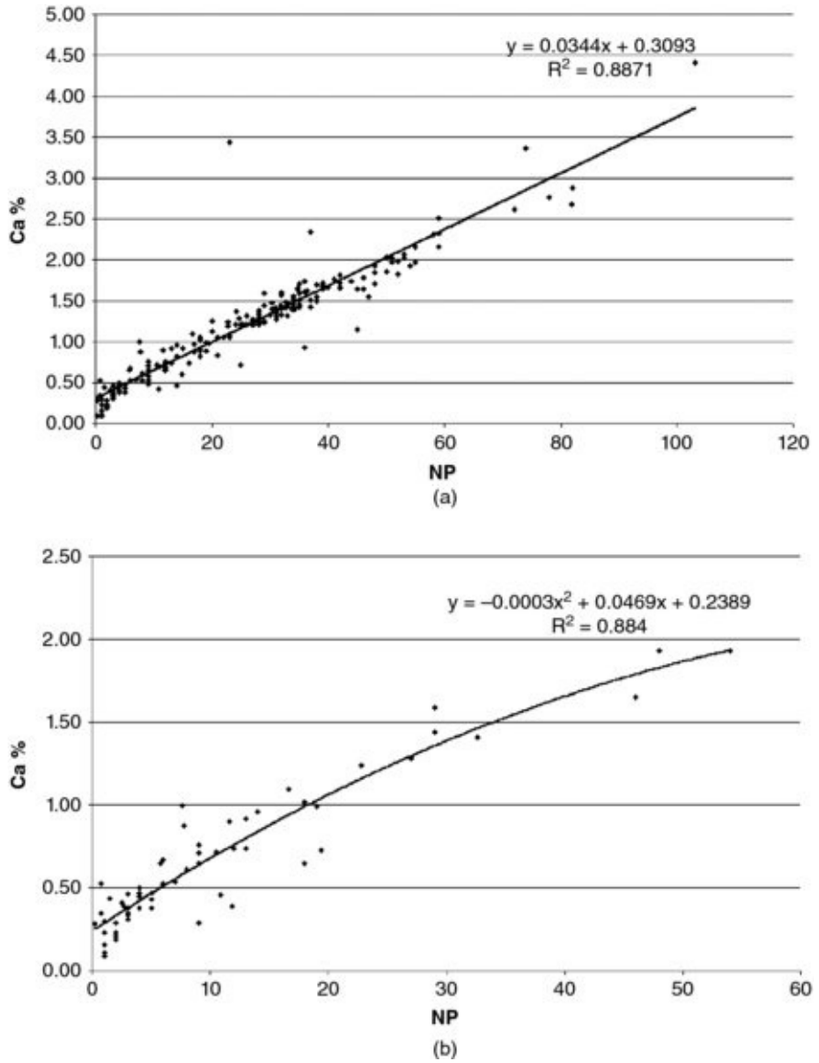


Figure 26.3 (a) Positive relationship between Ca and NP; (b) same relationship but with a different curve fitting.

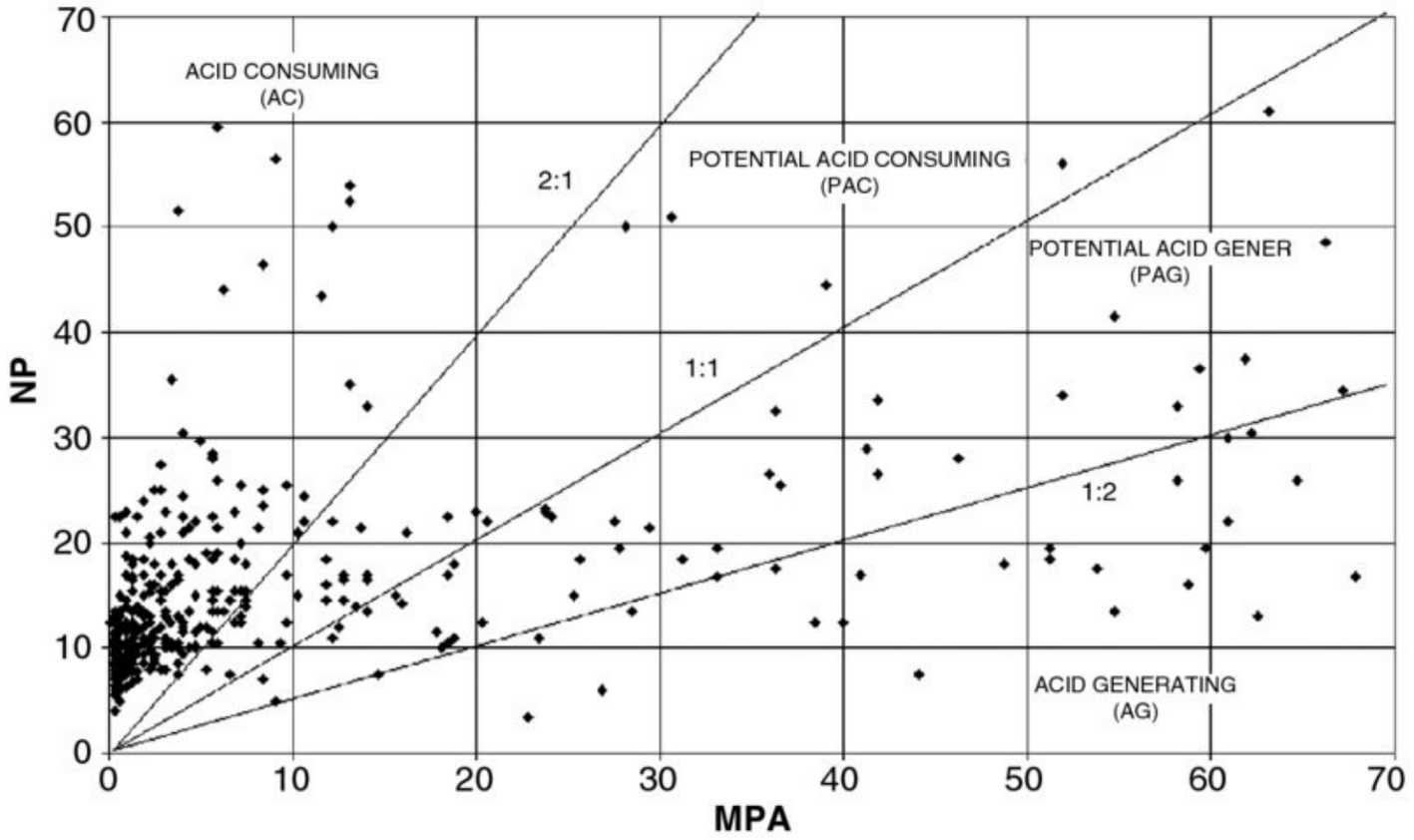


Figure 26.4 NP versus MPA.

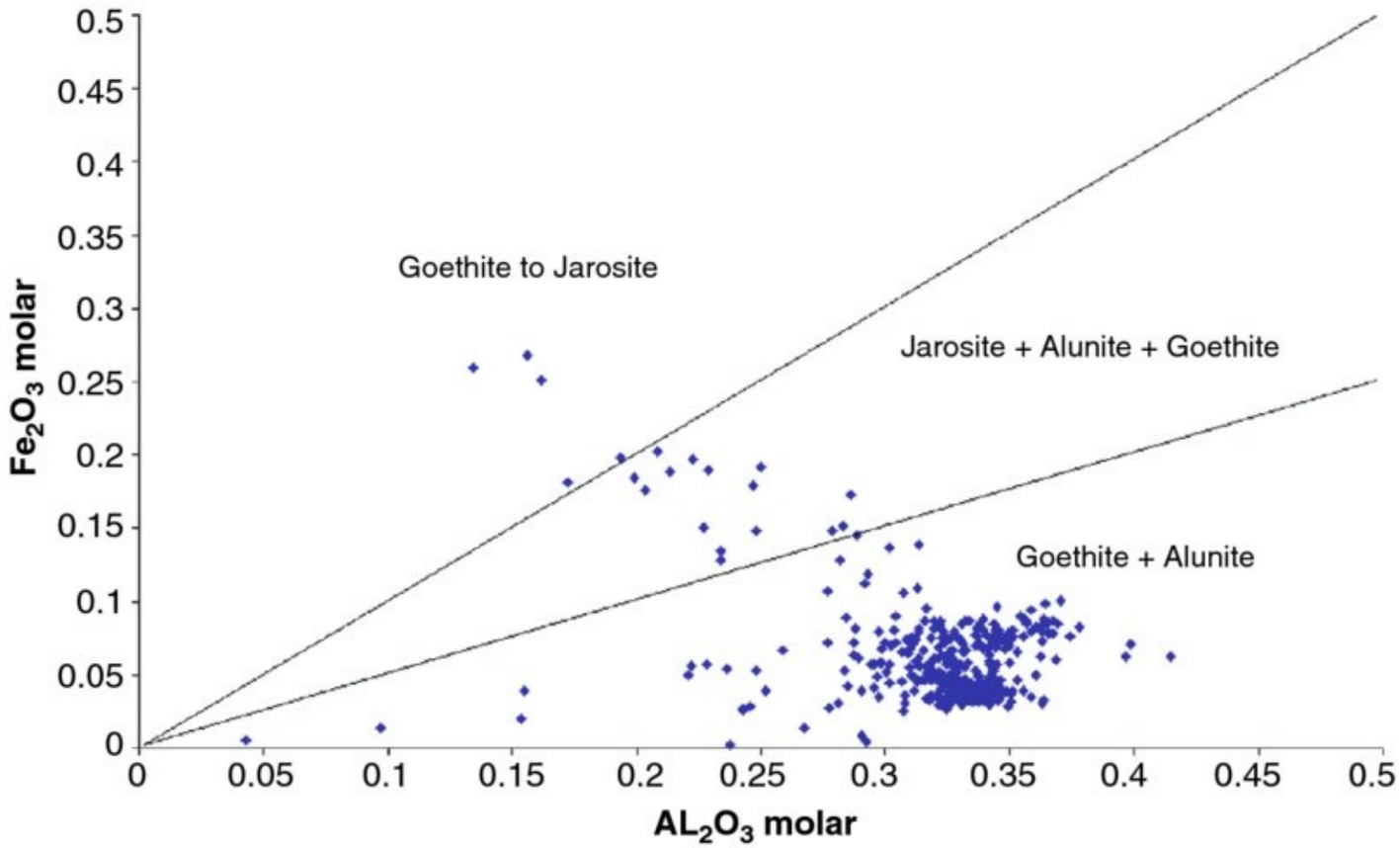


Figure 26.5 Fe (mol) versus Al (mol).

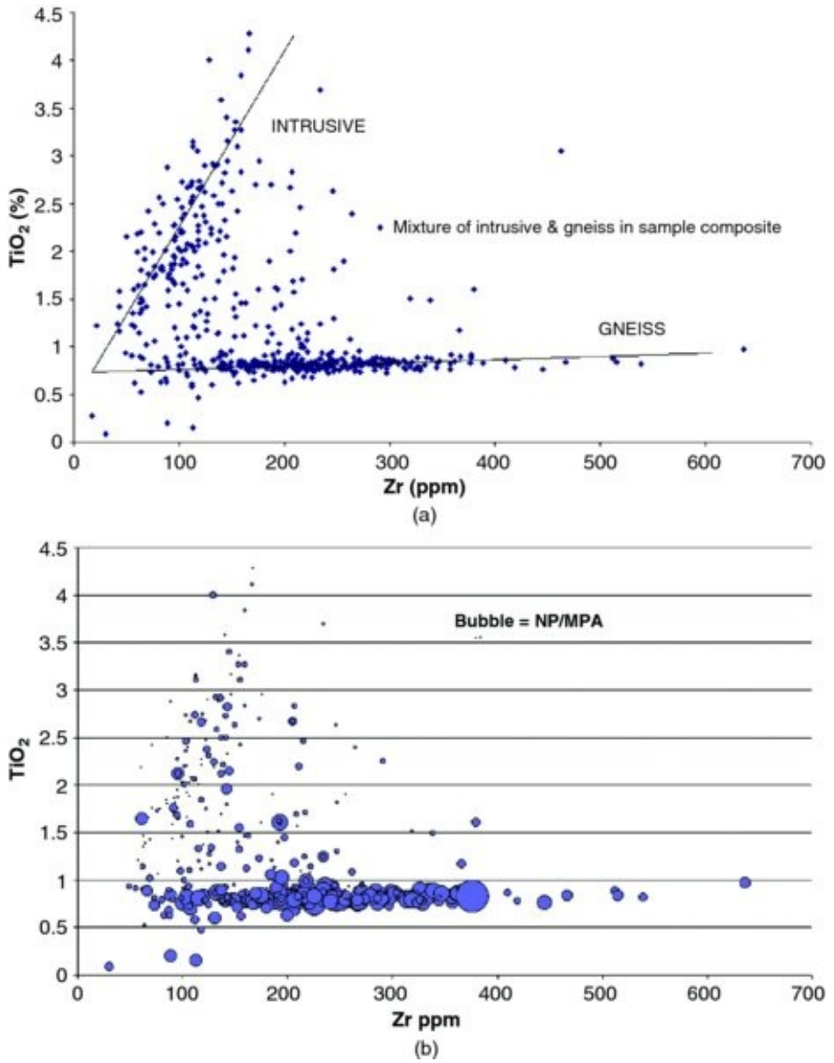


Figure 26.6 Rock type classification (TiO_2 vs. Zr).

Univariate Data Analysis

Univariate statistical methods are used to summarize individual parameter data (assuming a single population). Before univariate statistics are meaningful, the number of populations present must be established by plotting frequency (histograms) or probability plots. If a single population exists, its tendency to normality or lognormality must also be established. For a single population, the distribution parameters can be calculated (mean-arithmetic, geometric, mode, and median). However, one must be aware of incorporating very high numbers and background (detection levels) in the statistics, as they can produce skewed and misleading results.

Multivariate Data Analysis

Multivariate statistical methods are used to determine interrelationships between variables. This type of analysis includes correlation coefficients, factor analysis, cluster analysis, and discriminant analysis. Problems that arise in using these methods are:

1. Data below the laboratory detection limit create censored value distributions.
2. Multiple populations (e.g., AG, PAG, PAC) may be present.
3. The distribution of the variables may be nonnormal.

To define various statistical parameters, the different populations must be separated and analyzed individually. Logarithms of the data are often used because of the apparent lognormality of many geochemical distributions.

Geostatistical Analysis

Geostatistical methods are commonly used to determine the spatial relationships of individual elements in ore and waste rock resource calculations (Downing and Giroux, 1995, 2013).

Background and Threshold Data Analysis

Many variables measured in the course of baseline and environmental studies are continuous due to inherent geological or geochemical variability within a sample and from sample to sample. For example, 100 samples analyzed for neutralization potential (NP) might produce values ranging from 1 to 250 kg $CaCO_3$/metric ton. The variable NP is continuous between these limits because any intermediate value could be assumed by a sample. Also, due to errors inherent in sampling and analysis there is no discrete number that can define that variable, only an approximation, with the best number resulting from use of the standards within the analytical laboratory. Sampling variability is seldom examined in ARD studies. Unfortunately, many people accept the numbers from a laboratory and attempt to define the necessary criteria that regulators want in order to define the limits of acid generation to acid consumption. The concept of defining these limits must take into account the inherent geological and/or geochemical variability. An approach to this problem would be the determination (or selection) of threshold values. This concept is used by geochemists to determine the background and anomalous values of variables (Parslow, 2000; Sinclair, ,). This is a graphical method of analyzing variable distributions. This method has also been used to determine the background values between natural and anthropogenic sources (Runnells et al., 1998).

An MSDOS software program, Probability Plot (Stanley, 1998), is used for this analysis. This program is an interactive software tool that allows a user to rapidly analyze cumulative frequency data. This analysis takes the form of a modeling exercise, comparing the actual cumulative frequency distribution with a theoretical frequency distribution model. This model is both flexible, in that it is capable of representing numerous forms of frequency distributions consisting of combinations (mixtures) of normal (or lognormal) component populations, and restrictive, in that it cannot represent other distribution forms commonly encountered in cumulative frequency data (such as Poisson, exponential, or binomial distributions).

The user should remember that probability plot analysis is merely a comparison of an actual cumulative frequency distribution and a theoretical distribution model. Use of this program implies or requires that the user assume that the actual data are distributed in the same form as that of the theoretical model. If this assumption is not met (at least to some degree), the program will be of little help in understanding the data. A successful or appropriate frequency distribution model can be used to decompose multimodal data distribution into its component populations. These, in turn, can be used to define thresholds that separate the data into groups corresponding to these component populations.

This type of data analysis is useful for:

1. Determining of the number of populations from observations of both histograms and cumulative plots by optimizing this frequency distribution model and decomposing the data distribution into its component populations. This can be done by using normal and/or lognormal data. When two or more populations occur, the characteristics of each population need to be determined (i.e., mineralogy, geochemistry).

2. Modeling the cumulative plots to determine the relative percentage of each population by determining the general form of the theoretical frequency distribution model.
3. Determining the threshold values for each population by selecting thresholds to partition the data into groups representative of these component populations.

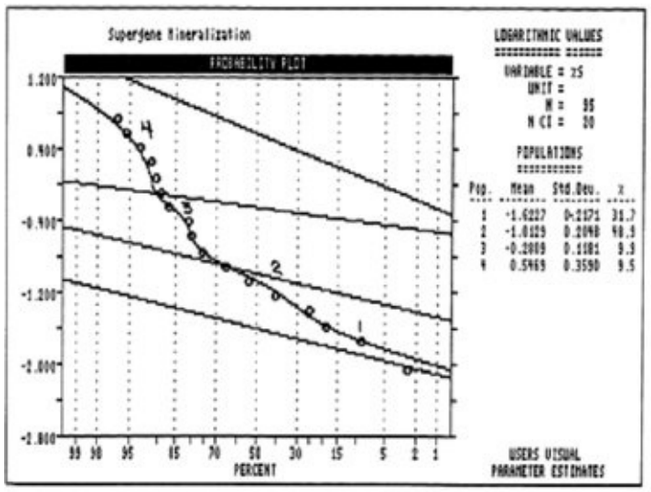
Case Study

Data for this case come from a porphyry copper–gold deposit that contains both supergene and hypogene mineralization. The following analysis was conducted:

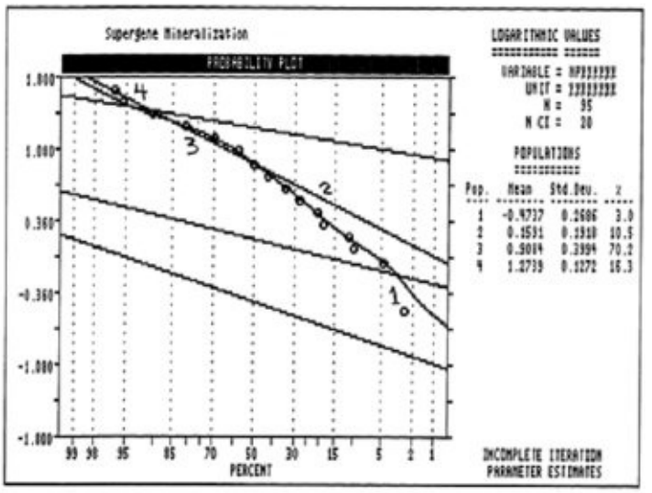
- Arithmetic and logarithmic histograms and cumulative plots were constructed.
- Plots were examined for populations and inflection points noted.
- Populations were divided and modeled:
  - Supergene (Figure 26.7a to c)
  - Hypogene (Figure 26.7d to g)
- Statistical and threshold values were determined for each population (Figure 26.8).
- Possible characteristics were determined for each population:
  - Sampling
    - More samples were taken for a particular rock or mineralization type.
    - More samples were taken in a high-grade zone than for either low-grade or waste rock.
  - Grade
    - Cutoff
    - Low grade
    - High grade
  - Neutralizing minerals
    - Short term (carbonate)
    - Long term (silicate)
  - Acid-generating minerals
    - Fast (pyrite)
    - Slow (chalcopyrite)
  - Mineralogy
    - Gangue minerals
    - Ore minerals
    - Alteration minerals
  - Rock types
  - Lithogeochemistry (see Downing and Madiesky, 2013)

- Trace elements (see Downing and Gravel, 1993)

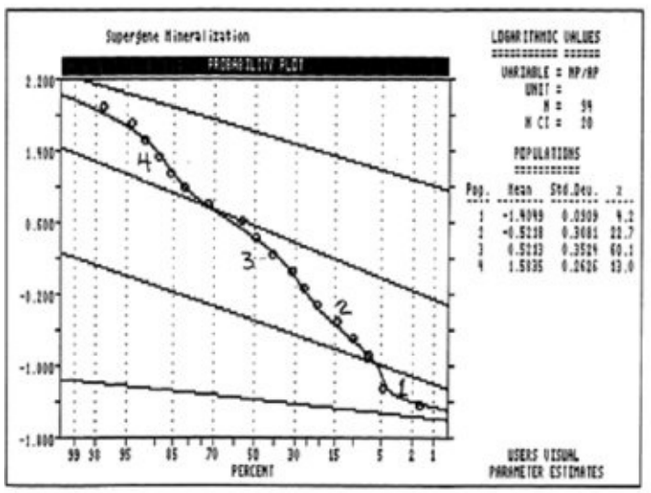
- Site-specific threshold values were determined for:
  - Acid-generating material
  - Potentially acid-generating material
  - Potentially acid-consuming material
  - Acid-consuming material



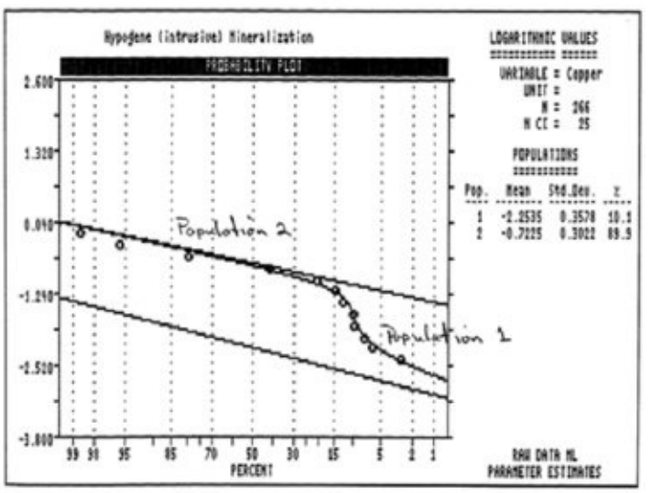
(a)



(b)



(c)



(d)

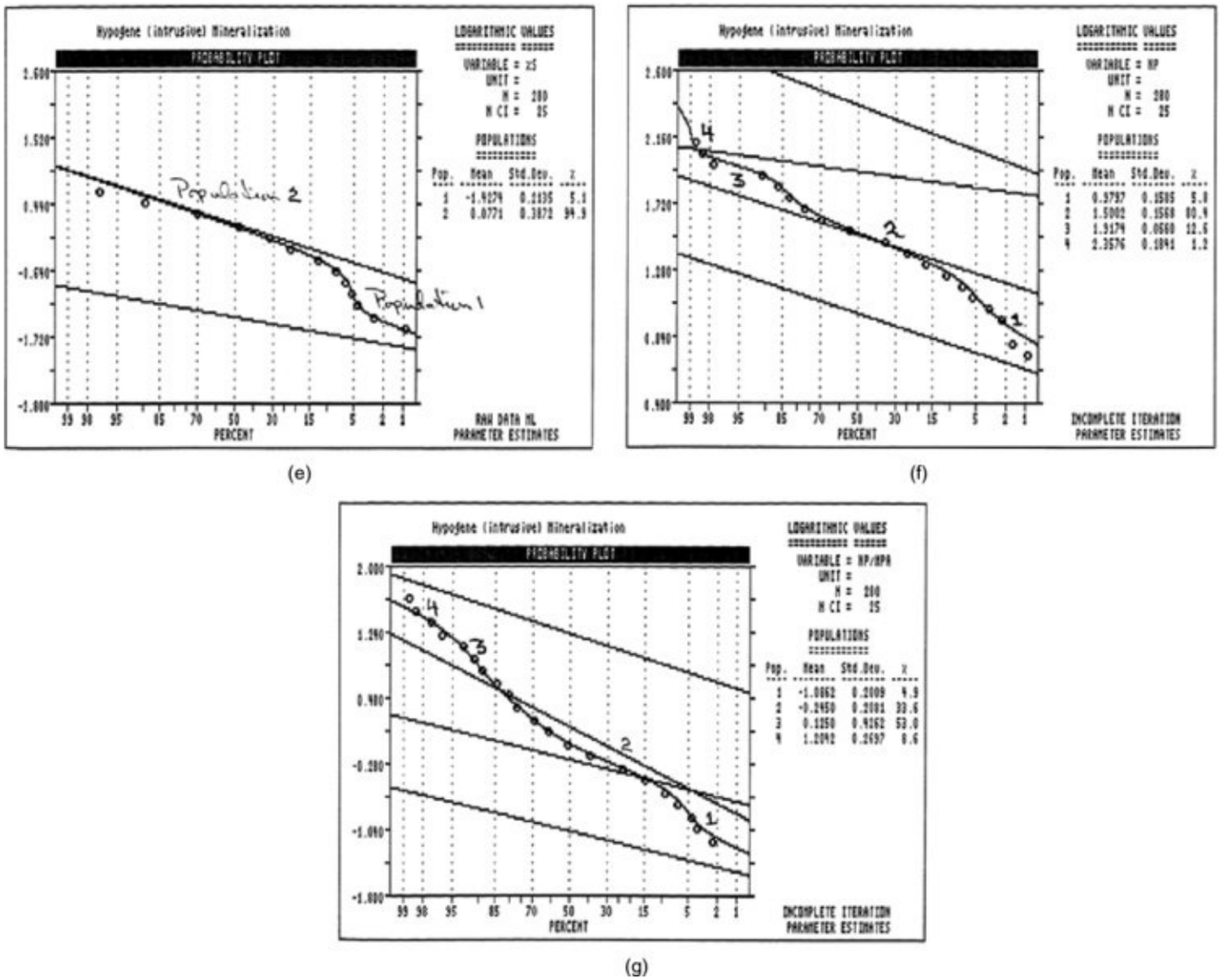


Figure 26.7 (a) Supergene 1; (b) supergene 2; (c) supergene 3; (d) hypogene 4; (e) hypogene 5; (f) hypogene 6; (g) hypogene 7.

The results are summarized in Figure 26.8.

TABLE1: SUMMARY OF DATA																		
HYPOGENE MINERALIZATION																		
	Number of Samples = 280																	
	Number of class intervals = 280																	
	Range	Number		Population 1				Population 2				Population 3				Population 4		
		Population	average	thresholds	%	Classification	average	thresholds	%	Classification	average	thresholds	%	Classification	average	thresholds	%	Classification
				lower - upper				lower - upper				lower - upper				lower - upper		
Cu (%)	0.031-0.843	2	0.006	0.001 - 0.029	10.14	low grade	0.189	0.047 - 0.762	89.86	high grade								
S (%)	0.022-5.760	2	0.043	0.016 - 0.115	5.23	low	1.158	0.201 - 6.682	94.77	high								
NP		4	9.54	4.60 - 19.80	5.84	low	31.68	15.37 - 65.15	80.36	low	82.69	61.03 - 112.04	12.57	moderate	227.84	97.58 - 531.97	1.24	high
NP / MPA		4	0.082	0.033 - 0.207	4.86	AG	0.569	0.218 - 1.484	33.55	PAG	1.333	0.187 - 9.491	53.01	PAC	16.002	4.622 - 55.405	6.57	AC
SUPERGENE MINERALIZATION																		
	Number of Samples = 95																	
	Number of class intervals = 20																	
	Range	Number		Population 1				Population 2				Population 3				Population 4		
		Population	average	thresholds	%		average	thresholds	%		average	thresholds	%		average	thresholds	%	
				lower - upper				lower - upper				lower - upper				lower - upper		
Cu (%)	0.009-1.495	ND	ND	ND	ND		ND	ND	ND									
S (%)	0.007-9.700	4	0.026	0.008-0.089	32.29	oxide zone	0.093	0.033-0.261	48.35		0.527	0.326-0.853	9.54		3.852	0.893-16.613	9.82	
NP	0.25 - 54	4	0.336	0.098 - 1.157	3.01	negligible	1.442	0.596 - 3.488	10.48	low	8.098	1.287 - 50.945	70.2	moderate	18.789	10.458 - 33.756	16.31	high
NP / MPA	0.030-93.130	4	0.039	0.027 - 0.058	4.7	AG	0.359	0.088 - 1.463	22.29	PAG	3.542	0.582 - 21.544	62.17	PAC	43.395	3.125 - 143.47	10.84	AC

Figure 26.8 Summary of Data.

Supergene

Copper: Not determined

Sulfur: Four populations:

Population 1: very low sulfide content, very low sulfate content

Population 2: low sulfide content, low sulfate content

Population 3: moderate sulfide content, low-to-moderate sulfate content

Population 4: high sulfide content, high sulfate content

NP: Four populations (NP determination using the modified Sobek method):

Population 1: low carbonate content, very low noncarbonate gangue NP-contributing material

Population 2: low-to-moderate carbonate content, low noncarbonate gangue NP-contributing material

Population 3: moderate carbonate content, low noncarbonate gangue NP-contributing material

Population 4: high carbonate content, moderate noncarbonate gangue NP-contributing material

NP/MPA: Four populations:

Population 1: negligible carbonate content, no noncarbonate gangue material, high sulfide content

Population 2: low carbonate content, negligible noncarbonate gangue material, moderate sulfide content

Population 3: moderate carbonate content, low noncarbonate gangue material, low sulfide content

Population 4: high carbonate content, moderate noncarbonate gangue material, negligible sulfides

Conclusions:

- Not enough samples have been taken to properly characterize low-grade ore from waste rock material for copper grade. This will also affect the sulfur and NP populations.

- Sulfides are pyrite/marcasite, chalcopyrite, bornite, trace galena, and sphalerite.
- The sulfate content is due to barite, gypsum, jarosite, and melanterite.
- Each sample within a specific population must be identified in the field, as that particular population may have some aerial context (i.e., oxide zone overlying the supergene zone).
- The NP curve is not as definitive as the NP/MPA curve regarding the populations.

Hypogene

Copper: Two populations:

Population 1: low grade (includes waste rock)

Population 2: high grade

Sulfur: Two populations:

Population 1: low-grade copper content, high pyrite content (waste rock to low grade ore)

Population 2: high-grade copper content, low pyrite content

NP: Four populations (NP determination using the modified Sobek method):

Population 1: negligible carbonate content, no noncarbonate gangue NP-contributing material

Population 2: low carbonate content, negligible noncarbonate gangue NP-contributing material

Population 3: moderate carbonate content, low noncarbonate gangue NP-contributing material

Population 4: high carbonate content, moderate noncarbonate gangue NP-contributing material

NP/MPA: Four populations:

Population 1: negligible carbonate content, no noncarbonate gangue material, high sulfide content

Population 2: low carbonate content, negligible noncarbonate gangue material, moderate sulfide content

Population 3: moderate carbonate content, low noncarbonate gangue material, low sulfide content

Population 4: high carbonate content, moderate noncarbonate gangue material, negligible sulfides

Conclusions:

- Not enough samples have been taken to characterize low-grade ore properly from waste rock material for copper grade. This will also affect the sulfur and NP populations.
- 86% of the samples have low NP values (populations 1 and 2).
- 10% of the samples have an NP/MPA ratio above 4.
- Mixing of supergene and hypogene material is highly dependent on segregation into populations that may not be economically feasible.
- Mixing of hypogene material is highly dependent on segregation into populations and tonnage of each material.

Error Analysis

Errors associated with sampling, inappropriate test procedures, tests run incorrectly, and chemical analysis may all be difficult to define, measure, and analyze. Precision and replication are parameters that deal with quality assurance/quality control (QA/QC) procedures and must be documented in any ARD report. The Thompson–Howarth (1976) technique is a rigorous statistical method of calculating the differences between duplicate data in order to determine precision. Errors also occur in differences of scale between test work and actual mine operations. This error will have far-reaching implications if not recognized and solved during test work and ARD mine planning.

Quality Assurance/Quality Control Analysis

The QA/QC aspect of data management and analysis of data has been discussed by Downing and Mills (1998b). Analysis and reporting of QA/QC is very important to provide assurances that the data are reliable.

Detection-Level Analysis

Determination of the accepted value when analytical results are reported as “at or below” detection level is important for sulfide (sulfur and sulfate analysis) and trace elements, and must be stated in the ARD report. One method is to use the detection level of the analytical method as the value; another method is to use half of the detection level as the value.

Lithogeochemical Data Analysis

The analysis of lithogeochemical data has been discussed in detail by Downing and Madeisky (1998). Lithogeochemical data are representative of the bulk chemistry (and hence the bulk mineralogy) of a sample and as such can be used to predict the characteristics of lithological units, weathering potential, alteration potential, and determination of the theoretical and empirical buffering capacities. This is the only method that takes into account the mineralogy and chemistry of a sample and is therefore representative of that sample's buffering capacity.

Particle Size Analysis

Particle size, particle size distribution, and individual mineral grain size are parameters that affect both acid generation and acid neutralization. These relationships are discussed by Mills (1988) and Scharer et al. (1974). Particle size analysis is a necessary aspect of any ARD study.

Probability Analysis

The ARD practitioner must eventually deal with several future possibilities: Will this material become acid generating? and When will it go acid? Probability analysis deals with both analytical and experimental data. The latter will give an approximation if rigorous experiments are conducted.

Computer Modeling Analysis

Computer modeling of geochemical data from acid-generating waste rock piles simulating geochemical processes to predict the quality of acid rock drainage has been discussed by Perkins et al. (). Various computer programs are reviewed based on five categories: equilibrium models, mass-transfer modes, coupled mass-transfer flow models, supporting modes, and empirical and engineering models. These models can be used to improve the understanding of interactions between geochemical processes and to perform comparisons between decommissioning scenarios.

Computer models for predicting water quality from waste rock piles, tailings impoundments, and open pits may use some computer programs in conjunction with hydrogeological models. An approach to modeling pit filling and pit lake chemistry on mine closure has been discussed by Bursey et al. (1997). Numerous papers have been presented regarding computer modeling for predicting water geochemistry (Alpers and Nordstrom, 1999; Maest and Kuipers, 2005). As with all computer modeling, care must be taken that the ARD practitioner understands the program and its capabilities, including data input and results predicted.

Geoenvironmental Analysis

As ARD is essentially controlled by bedrock geology, an understanding of the geological environment is extremely important. Conceptual models for ore formation and mineralization provide ARD practitioners and regulators with some ideas as to the potential size of metal leaching and mobility from both a natural (premining) and an anthropogenic (mining) context. This concept has been discussed by Alpers and Nordstrom () and Kwong (1970). This concept is equally important for understanding mineralized bedrock where no metal mining is practical and ARD material is excavated for construction purposes. Data analysis in this aspect includes good data collection and rigorous interpretation(s) as to understanding background values and establishing thresholds.

Costs

The cost of an ARD study is a major component in the environmental survey. Cost has a far-ranging impact on the mining plan, reclamation, and closure. It is necessary to conduct a thorough study and collect quality data that can be used with confidence by mining engineers. This also has a profound impact on the acceptance of the ARD study by regulators and the public. No ARD study should be compromised by an underachieving budget (i.e., the budget should not predetermine the thoroughness of the study). Costs associated with data collection include (1) sampling, (2) quality control, (3) additional data analyses, and (4) compilation and database management, interpretation, and reporting.

Visual plots should be a major component of all reports, as they show the reader the distribution of particular parameters from which interpretations are made. They also provide some assurance to the reader that the ARD practitioner has conducted a credible data analysis and that interpretations are backed up with data plots. Each study may be site-specific, but the data analysis routines are the same.

References and Suggested Reading

Alpers, C.N., and Nordstrom, D.K., 1999. Geochemical Modeling of Water-Rock Interactions in Mining Environments. In: G.S. Plumlee and M.J. Logsdon (eds.), The Environmental Geochemistry of Mineral Deposits, Part A: Processes, Techniques and Health Issues, Reviews in Economic Geology, Society of Economic Geologists, Inc., vol. 6A, pp. 289--324.

Alpers, C.N., and Nordstrom, D.K., 2000. Estimation of pre-mining conditions for trace metal mobility in mineralized areas: an overview. In: Proceedings of the 5th International Conference on Acid Rock Drainage (ICARD 2000), Society of Minerals and Metals Exploration, Littleton, CO, pp. 463–472.

Bellefontaine, K., and Price, W. A., 2006. Environmental Management Plans: A Key Tool in Ensuring Successful Long-Term Environmental Management at Closed Mine Sites with ML/ARD. In: Proceedings of 7th International Conference on Acid Rock Drainage, St. Louis, Missouri, March 26--30.

Bladh, K., 1992. The formation of goethite, jarosite and alunite during the weathering of sulfide-bearing felsic rocks. Economic Geology, Vol. 77, pp. 176–184.

Bursey, G.G., Mahoney, J.J., Gale, J.E., Dignard, S.E., Napier, W., Riehm, D., and Downing, B., 1997. Approach used to model pit filling and pit lake chemistry on mine closure, Voisey's Bay, Labrador, reprint. In: Proceedings of the 4th International Conference on Acid Rock Drainage, Vancouver, BC, Canada, May, 23 pp.

Day, S., 1995. Evaluation of static testing techniques, Kudz Ze Kayah Project, Yukon Territory. Summary Notes, MEND Prediction Workshop, December 7–8.

Day, S., Coulter,G., and Falutsu, M., 2000. Geochemical studies to characterize the complex sulfur mineralogy at Red-Dog Pb–Zn mine. In: Proceedings of the 5th International Conference on Acid Rock Drainage, May, pp. 683–691.

Downing, B.W., and Giroux, G., 1993. Estimation of a waste rock ARD block model for the Windy Craggy massive sulfide deposit, northwestern British Columbia. Exploration and Mining Geology, vol. 2, No. 3, pp. 203–215.

Downing, B.W., and Giroux, G., 2013. Acid rock drainage waste rock block modeling. Published on the ARD website, www.enviromine.com/ard.

Downing, B.W., and Gravel, J., 1998. Trace Element Geochemistry in Acid Rock Drainage. Paper published on the ARD website, 14 pp.

Downing, B.W., and Madeisky, H.E., 1998. Lithogeochemical methods for acid rock drainage studies and prediction. Exploration and Mining Geology, Vol. 6, no. 4.

Downing, B.W., and Mills, C., 1998a. Trace element geochemistry in acid rock drainage. Published on the ARD website, www.enviromine.com/ard.

Downing, B.W., and Mills, C., 1998b. Quality assurance/quality control in ARD testwork. Published on the ARD website, www.enviromine.com/ard.

Garrett, R.G., Kane, V.E., and Zeigler, R.K., 1980. The management and analysis of regional geochemical data. Journal of Geochemical Exploration, Vol. 13, pp. 115–152.

Jambor, J.L., Dutrizac, J.E., and Chen, T.T., 2000. Contribution of specific minerals in the neutralization potential in static tests. In: Proceedings of the 5th International Conference on Acid Rock Drainage, May, pp. 551–561.

Koch, G.S., Jr., and Link, R.F., 1970. Statistical Analysis of Geological Data. Wiley, New York, 374 pp.

Kurzl, H., 1988. Exploratory data analysis: recent advances for the interpretation of geochemical data. Journal of Exploration Geochemistry, Vol. 30, pp. 309–322.

Kwong, J., 2000. Thoughts on ways to improve acid rock drainage and metal leaching prediction for metal mines. In: Proceedings of the 5th International Conference on Acid Rock Drainage, May, pp. 675–682.

Maest, A.S., and Kuipers, J. R., 2005. Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties and State-of-the-Art. Earthworks, Washington, DC.

Mills, C., 1998. Particle size distribution and liberation size. Published on the ARD website, www.enviromine.com/ard.

Parslow, G.R., 1974. Determination of background and threshold in exploration geochemistry. Journal of Geochemical Exploration, vol. 3, pp. 319–336.

Perkins, E.H., Nesbitt, H.W., Gunter, W.D., St.-Arnaud, L.C., and Mycroft, J.R., 1995. Critical Review of Geochemical Processes and Geochemical Models Adaptable for Prediction of Acidic Drainage from Waste Rock. MEND Project Report 1.42.1. MEND, Ottawa, ON, Canada.

Price, W.A., and Kwong, Y.T.J., 1997. Waste Rock Weathering, Sampling and Analysis: Observations from the British Columbia Ministry of Employment and Investment Database. In: Proceedings of 4th International Conference on Acid Rock Drainage, Vancouver, vol 1, pp. 31--46.

Price, W.A., and Errington, J., 1998. Guidelines for Metal Leaching and Acid Rock Drainage at Minesites in British Columbia, British Columbia Ministry of Energy and Mines, 86 pp.

Runnels, D.O., Dupon, D.P., Jones, R.L., and Cline, O.J., 1998. Determination of natural background concentrations of dissolved components in water at mining, milling and smelting sites. Mining Engineering, February, pp. 65–71.

Scharer, J.M., Bolduc, L., Pettit, C.M., and Halbert, B.E., 2000. Limitations of acid-base accounting for predicting acid rock drainage. In: Proceedings of the 5th International Conference on Acid Rock Drainage, May, pp. 591–601.

Shaw, S., and Mills, C., 1998. Petrology and mineralogy in ARD prediction. Published on the ARD website, www.enviromine.com/ard.

Sinclair, A.J., 1974. Selection of threshold values in geochemical data using probability graphs. Journal of Geochemical Exploration, Vol. 3, pp. 129–149.

Sinclair, A.J., 1991. A fundamental approach to threshold estimation in exploration geochemistry: probability plots revisited. Journal of Geochemical Exploration, vol. 41, pp. 11–22.

Stanley, C., 1987. Probplot, Special Volume 14. Association of Exploration Geochemists, Nepean, ON, Canada.

Thompson, M., and Howarth, R.J., 1978. A new approach to the estimation of analytical precision. Journal of Geochemical Exploration, vol. 9, pp. 23–30.

27
Acid Generation and Drainage Workshop: Example Calculations and Solved Problems

JEFF SKOUSEN, PAUL ZIEMKIEWICZ, AND JAMES A. JACOBS

This chapter comprises a series of example calculations associated with acid-drainage evaluations, chemical neutralization operations, and water flow estimations that apply to field professionals, students, mine operators, and consultants. Many of these calculations can be used for acid sulfate soils as well. Selecting the number of representative calculations and problems with the answers is critical for a successful field project.

Planning the Overburden Analysis

The number of soil or rock borings and samples needed to characterize the acid generation potential at a site accurately must be determined. Overburden analysis can be used as one of the tools in the prediction of mine drainage quality. One of the issues is to determine the number of samples to collect in the field for the overburden analysis. The number of boreholes should reflect the stratigraphic complexity of the site, the site shape, and the availability of other geochemical data. The number of boreholes should be designed to encounter representative and typical lithological sections on the property.

Based on local conditions or experience, hardrock mines and acid sulfate soil locations will have their own practices for the number of boreholes, and different areas will also show variations in the number of boreholes needed to characterize the acid potential of a coal seam or of the overburden and waste materials. Below is a calculation of the number of boreholes for a Pennsylvania coal mine. More information on the borehole count is available (Brady et al., 1994; Tarrantino and Shaffer, 1998).

Assumptions Regarding the Example Problems

Minimum number of boreholes: 2

Number of acres mined:

1–49:	add 0	total boreholes	= 0 + 2
			= 2 boreholes
50–149:	add 1	total boreholes	= 1 + 2
			= 3 boreholes
150–249:	add 2	total boreholes	= 2 + 2
			= 4 boreholes
250–349:	add 3	total boreholes	= 3 + 2
			= 5 boreholes

Example Assume that no previous data are available. A site with 100 acres would require 3 boreholes = 1 (add) + 2 (min.) = 3 boreholes.

Workshop Problems

Problems are scattered throughout the chapter identified by a "P" preceding a double number: e.g., P27.1.

P27.1. Assuming that no geochemical data are available, how many boreholes would be required if the planned coal mine is 172 acres? Provide your answer in boreholes per hectare. Convert the 172 acres into hectares (1 acre = 0.404 ha).

Answer: 4 boreholes for 69.5 ha. Explanation: Using the assumptions outlined above, the minimum number is 2 boreholes, so for 150 to 249 acres, 2 boreholes are added, for a total of 4 boreholes for 172 acres. Convert 172 acres into hectares = 172 acres × 0.404 ha/acre = 69.5 ha.

P27.2. If complete data from 10 boreholes in a potential coal mining area of 25 acres were available, how many additional samples or boreholes would you drill?

Answer: Using the assumptions listed above, none; only 2 cores would be necessary for 25 acres.

P27.3. Assume that the overburden rocks were cored and logged continuously for lithological characteristics and thickness, and evaluated as to pH. Assume that the tons of crushed limestone equivalent per 1000 tons of overburden material has been calculated for total sulfur (%), maximum percent total sulfur (acid potential), and excess or deficiency per ton of crushed limestone per 1000 tons of overburden material. How many additional borings would you drill?

Answer: None; 2 borings with continuous coring for 25 acres is adequate.

P27.4. What budget would be needed for a drilling program of ten 150-ft borings? Assume that the cost of drilling is $10 per foot drilled, $2000 per boring for chemical analyses, and $350 for a drilling permit for the entire project. Assume that the professional time (geologists and engineers) is not included in the budget.

Answer: The total drilling project cost = drilling cost + laboratory cost + permit fees. Therefore, 10 borings to a target depth of 150 ft each = 1500 ft at $10/ft = $15,000 for the drilling budget:

$$\$15{,}000 + 10(\$2000) + \$350 = \$35{,}350.$$

Acid–Base Accounting Concepts

Acid–base accounting (ABA) is a method commonly used to characterize rock and soil overburden geochemistry. The purpose of performing ABA on a rock or soil sample is to identify the acid-producing potential due to the pyrite and other soluble sulfur minerals and the neutralization-producing potential due to alkaline materials, such as rock carbonates: limestone, dolomite, and calcareous-rich sediments. According to Smith and Sobek (1978) and Sobek (1987), the difference between the two potentials (acid potential and neutralization potential) indicates whether there is enough base (carbonate) naturally present in the rock or soil to neutralize all the sulfuric acid produced from the oxidation of pyrite (Evangelou, 1998).

Originally developed for the coal industry in the 1970s, ABA methods are best used in conjunction with a variety of other geochemical tests and integrating the data into detailed lithological characterization studies, and developing site conceptual models provides better results for predicting acid generation. An example of acid–base accounting is shown in Table 27.1. Most of the information and data are collected as observations in the field (i.e., lithological characterization) or measurements made in the laboratory [i.e., percent sulfur (%S); neutralization potential (NP)]. Plotting detailed lithological information with

ABA data (Figure 27.1) shows some of the geochemical properties of the rocks that will be disturbed if mining of the coal seam were to proceed.

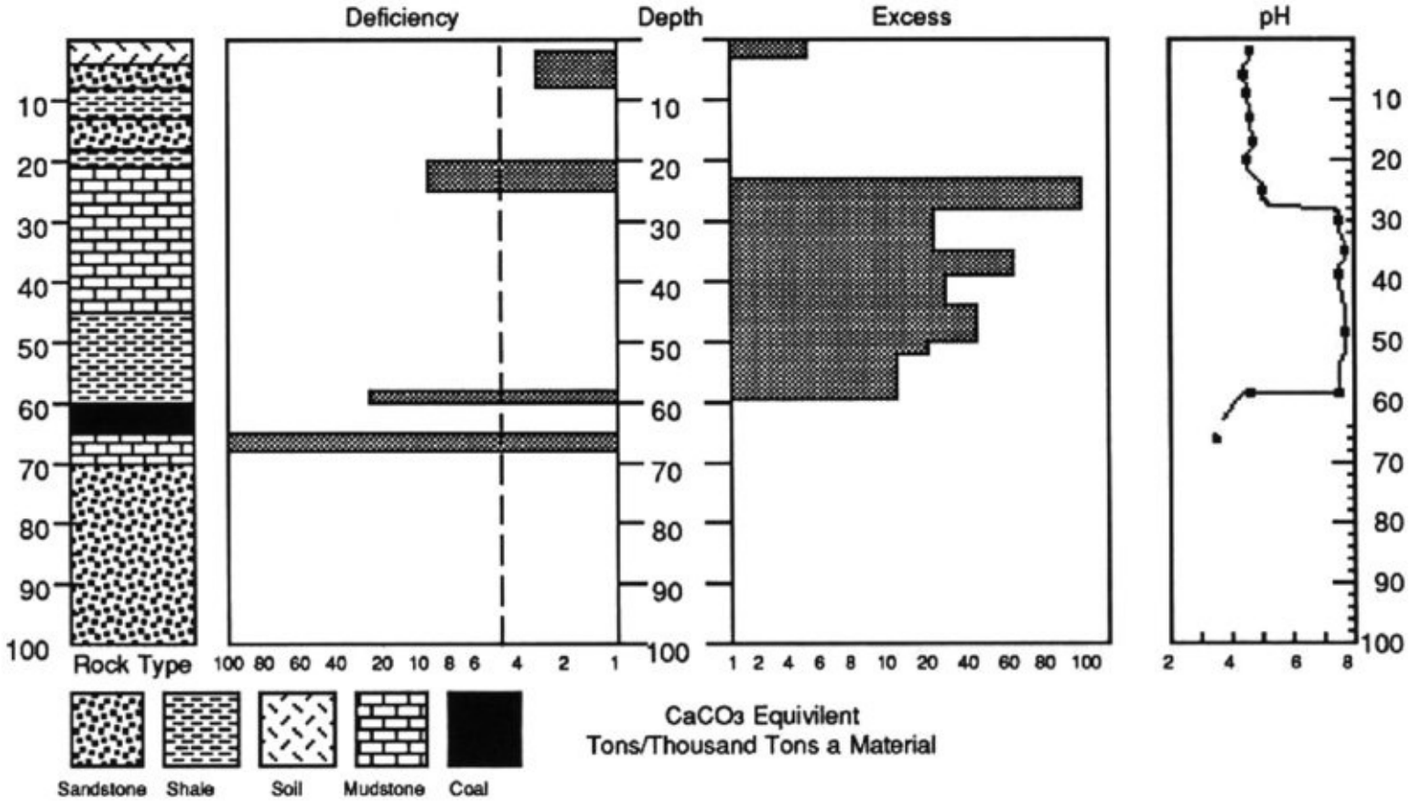


Figure 27.1 Graphic representation of overburden properties as measured by acid–base accounting. Shows 100 ft of section, including 0 to 67 ft of the data from Table 27.1.

Table 27.1 Example of an Acid–Base Account[a]

						$CaCO_3$ Equivalent (tons/1000 tons of material)				
Sample Number	**Bottom Depth (feet)**	**Rock Type**	**Fizz**	**Color**	**%S**	**Max. from %S**	**Amount Present (NP)**	**Max. Needed (pH 7)**	**Excess**	**Paste pH**
1	3	Soil	0	7/3	0.035	1.09	3.52	—	2.53	4.4
2	6	SS	0	8/6	0.029	0.91	−1.51	2.42	—	4.3
3	6	SS	0	8/2	0.023	0.72	−1.59	2.31	—	4.6
4	14	SH	0	7/4	0.009	0.28	−0.60	0.88	—	4.6
5	17	SS	0	7/4	0.009	0.28	−0.09	0.37	—	4.7
6	20	SH	0	8/3	0.011	0.34	−0.17	0.51	—	4.5
7	24	MS	0	7/1	0.263	8.22	−0.94	9.16	—	4.8
8	28	MS	1	7/1	0.179	5.59	78.33	—	72.74	7.8
9	35	MS	0	7/1	0.028	0.88	15.77	—	14.89	7.9
10	39	MS	1	7/0	0.140	4.38	39.71	—	35.33	7.8
11	55	MS	1	7/1	0.278	8.69	25.25	—	16.56	8.0
12	49	SH	1	7/1	0.079	2.47	25.76	—	23.29	8.1
13	51	MS	1	7/1	0.665	20.78	32.45	—	11.67	7.9
14	44	SH	1	7/1	0.610	19.06	25.88	—	6.82	7.8
15	58	SH	0	6/1	0.355	11.09	17.78	—	6.69	7.3
16	59	SH	0	4/1	0.800	25.00	3.80	21.20	—	4.2
17	64	Coal								
18	67	MS	0	6/1	2.820	88.12	−2.78	90.90	—	3.5

[a]Each major lithological layer in the overburden rock sequence is broken out by horizontal thickness.

The role of carbonate is important when predicting acid mine drainage. The neutralization potential (NP) was found to be a much better predictor of whether a potential coal mine would produce alkaline or acidic water than was the maximum potential acidity (MPA), calculated from the overburden sulfur content (Brady and Hornberger, 1990; Brady et al., 1994; Perry and Brady, 1995). MPA was shown to be an unreliable predictor of acid generation potential, but a study (diPretoro, 1986) found that net neutralization potential (NNP) and NP were the best predictors of acid drainage quality for the Appalachian coal mine sites studied. Net neutralization potential is defined (Strock, 1998) as

$$\mathrm{NNP} = \mathrm{NP} - \mathrm{MPA}$$

Based on the work of Singer and Stumm (1970), the following reaction is used to describe pyrite oxidation:

$$FeS_2 + 3\tfrac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

P27.5. Assuming that crushed limestone [calcium carbonate ($CaCO_3$)] will be added to neutralize the acid in the reaction above, write a balanced reation between the products listed above and calcium carbonate.

Answer:

$$3Ca(OH)_2 + 6H^+ + 1\tfrac{1}{2}O_2 + Fe_2(SO_4)_3 = 3CaSO_4 + 3H_2O + 2Fe(OH)_3$$

ABA Calculations

Based on the local geology of the coal mining area, assume that an overall NNP greater than 12 ppt (parts per thousand) $CaCO_3$ or an NP greater than 22 ppt $CaCO_3$ is very likely to assure alkaline drainage. Based on these data, a conservative approach to determining alkaline addition rates would require application of alkaline material at a rate equal to the difference between an overall NNP of 12 ppt $CaCO_3$ or an NP of 22 ppt $CaCO_3$ and the actual premining overall NP or NNP. A site having an NNP of 2 ppt $CaCO_3$, for example, would require the application of an additional 1% $CaCO_3$. A safe level of alkaline addition would bring the NP value above 9 ppt $CaCO_3$ or the NNP above 6 ppt $CaCO_3$ (Smith and Brady, 1998). An example ABA calculation follows.

Tons of overburden:	500,000 [453,592 metric tons (mt)]
Acres of mining:	10 (4.05 ha)
Average net NP:	2 ppt $CaCO_3$
Deficiency:	(12 − 2) ppt $CaCO_3$ =
10 ppt $CaCO_3$:	1%

Tons additional NP required for net NP of 12: 1% × 500,000 tons overburden = 5000 tons (4536 mt)

Tons per acre required: 5000 tons/10 acres: 500 tons/ac (1120 mt/ha)

Adjusted for alkaline material with 80% $CaCO_3$ equivalent: 500 tons/ac ÷ 80% = 625 tons/ac (1200 mt/ha)

ABA Example

P27.6. Assume a proposed premining NP value of 9 ppt $CaCO_3$ and an average neutralization potential of 4 ppt $CaCO_3$, How much additional alkaline material with 80% $CaCO_3$ equivalent is needed? State your answer in tons/ac and mt/ha.

Tons of overburden:	1,275,000 (1,156,661 mt)
Acres of mining:	50 (20.2 ha)
Average net NP:	4 ppt $CaCO_3$
Deficiency:	(9 − 4) ppt $CaCO_3$
	5 ppt $CaCO_3$ = 0.5%

Tons of additional NP required for net NP of 9:

Answer:

$$5\% \times 1{,}275{,}000 \text{ tons overburden} = 63{,}750 \text{ tons (25,755 mt)}$$

Tons per acre required:

$$= \frac{63{,}750 \text{ tons}}{50 \text{ acres}} = 1275 \text{ tons/ac (3156 mt/ha)}$$

Adjusted for alkaline material with 80% $CaCO_3$ equivalent:

$$\frac{1275 \text{ tons/ac}}{80\%} = 1594 \text{ tons/ac (3945 mt/ha)}$$

Cost Comparison

The practicality of alkaline addition as a means of preventing acid drainage formation depends largely on economics. Important questions to ask include how much alkaline material is needed and its cost, transportation costs, and the added cost of incorporating the alkaline material into the backfill—all costs that can vary widely from site to site. In many cases these costs can determine whether or not a site can be mined. But assuming that a site could be permitted for mining with or without alkaline addition, it is also useful to examine the costs that would be avoided if alkaline addition were used in lieu of treatment of a long-term discharge of acid mine drainage. To perform this analysis, several assumptions must be made about the expected postmining drainage quantity and quality, with and without alkaline addition. Costs can then be estimated for long-term treatment and for alkaline addition.

The example that follows demonstrates this type of calculation for a 100-ac (40.5-ha) site which without alkaline addition would be expected to produce approximately 50 gal/min (3.2 l/s) of acidic drainage with a net acidity concentration of approximately 100 mg/L and an iron content of 20 mg/L. The flow rate is based on an expected annual recharge of 10 in. (25.4 cm) per year, typical for the northern Appalachians. ABA data indicate, however, the need for 500 tons/ac (1120 mt/ha) of alkaline material.

Cost of Alkaline Addition

$$100 \text{ ac at } 500 \text{ tons/ac} = 50{,}000 \text{ tons (45,455 mt) of alkaline material}$$

Cost of waste lime at $1/ton:	$ 45,455
Transportation at $8/ton:	363,640
Materials handling at $1/ton:	45,455
Total cost of alkaline addition:	$ 454,550

Treatment costs avoided: 50-year treatment costs for 50 gal/min (3.2 L/s) discharge, 100 mg/L acidity, 20 mg/L Fe estimated using the REMINE computer program (U.S. Enviornmental Protection Agency, 1988), and present value = 27.2 × annual cost: $1,183,445.

Net Neutralization Potential Calculation

Computation methods for NNP imply that acid generation from MPA and acid neutralization from NP take place concurrently and at equal rates. In fact, acid generation can proceed more rapidly and is catalyzed by *Thiobacillus ferrooxidans* and numerous other chemolithotrophic bacteria that metabolize sulfur. The solubilities of acid products are such that total acidity may range from hundreds to thousands of mg/L. Carbonate mineral dissolution is a function of pH and the partial pressure of carbon dioxide (Plummer et al., 1978) and does not occur as rapidly. Alkalinity in mine waters is seldom greater than 400 mg/L, due to the limited solubility of calcite and other carbonate minerals (Perry, 1998).

The traditional computation method for NNP utilizes MPA calculated from total sulfur × a 31.25 equivalence factor. Numerous modifications of the NNP calculation have been developed based on specific needs. Joseph et al. (1994) provided a summary of various ways of calculating NNP for both hydrological and agronomical interpretations. Some examples and applications follow.

$$\mathrm{NNP} = \mathrm{NP} - \mathrm{MPA}$$

where MPA is percent total sulfur × 31.25. The traditional method assumes that all sulfur is in a potentially acid-generating form and is usually appropriate for fresh unweathered overburden in Pennsylvania coal mining areas.

$$\mathrm{NNP} = \mathrm{NP} - \mathrm{PA}$$

Where PA is percent pyritic sulfur × 31.25. This method assumes that sulfide sulfur is the only acid-generating source; sulfate and organic sulfur are assumed to be non-acid generating. This is applicable where alkaline earth sulfate salts are present but is not applicable for metal sulfate salts.

$$\mathrm{NNP} = \mathrm{NP} - \mathrm{MPA}$$

Where MPA is percent total sulfur × 62.5 This assumes a closed system with no carbon dioxide gas removed from the system and where both sulfuric and carbonic acid must be neutralized.

$$\mathrm{NNP} = \mathrm{NP} - (\mathrm{PA} + \mathrm{EA})$$

Where PA is percent pyritic sulfur × 31.25 and EA is exchangeable acidity. This applies to soils and agronomic interpretations.

$$\mathrm{NNP} = \mathrm{NP} - (\mathrm{PA} + \mathrm{SMP})$$

Where PA is percent pyritic sulfur × 31.25, and SMP is the lime recommendation from buffer pH. This applies to soils and agronomic interpretations.

Calculations based on the traditional method are the most common method of computation in the coal-producing areas of Pennsylvania and other Appalachian states.

Estimating Water Flow

Once acid drainage is identified in streams and rivers, water flow can be calculated. Express your calculations in gallons per minute.

P27.7. Calculate the water flowing through a 90° V-notch weir that was 21 in. high in the weir. ($Q = 2.5H^{2.5}$), where Q is the flow in ft^3/s) and H is the height of the water in the weir (ft).

Answer:

$$10.13\ \text{ft}^3/\text{s or } 4546\ \text{gal/min}$$
$$21\ \text{in.} = 1.75\ \text{ft}$$
$$1\ \text{ft}^3/\text{s} = 448.8\ \text{gal/min}$$
$$Q = 2.5 \times 1.75\ \text{ft}^{2.5} = 10.13\ \text{ft}^3/\text{s}$$
$$10.13\ \text{ft}^3/\text{s} \times 448.8\ \text{gal/min}/(\text{ft}^3/\text{s})$$
$$= 4546\ \text{gal/min}$$

P27.8. Calculate the water flowing in a stream with four cross sections of 1-ft widths, depths of 0.3, 0.6, 0.9, and 1.2 ft, and velocities of 0.2, 0.5, 0.6, and 0.8 ft/s.

Answer: 1.86 ft^3/s or 835 gal/min.

P27.9. How many gallons of rainwater fell on a 100-ac watershed if it received 36 in. of rain during the year?

Answer:

$$1\ \text{ft}^3 = 7.48\ \text{gal}$$
$$100\ \text{ac} \times 43{,}560\ \text{ft}^2/\text{ac} \times 3\ \text{ft water}$$
$$= 13{,}068{,}000\ \text{ft}^3 \text{ or } 97{,}748{,}640\ \text{gal}$$

P27.10. Find the acidity of water (in mg/L $CaCO_3$ equivalent) that has the following characteristics: Fe^{3+} = 120 mg/L, Fe^{2+} = 60 mg/L, Al^{3+} = 100 mg/L, Mn^{2+} = 20 mg/L, and pH = 2.0.

Answer: 1520.5 mg/L as $CaCO_3$.

P27.11. A new coal mine being designed on Stinky Creek requires an acid mine drainage water treatment plant. Acidity control using hydrated lime and ammonia is being evaluated. The water flow is 3500 gal/min with 1250 mg/L acidity. Evaluate the cost of using hydrated lime at $275/ton (the conversion factor is 0.74), with the alternative of ammonia, which costs $1000/ton (conversion factor is 0.34). A factor of 0.0022 converts gal/min times mg/L (parts per million) acidity into tons of acidity per year. Assume that labor and mixing equipment costs are similar for acidity control using either the hydrated lime or ammonia option.

Answer: 3500 gal/min × 1250 mg/L acidity × 0.0022 conversion factor = 9625 tons of acidity per year.

Hydrated lime $(CaOH)_2$ option: cost-effective reagent but requires mixing:

$$9625\ \text{tons acidity/yr} \times 0.74\ \text{(conversion factor)}$$
$$\times\ \$275 = \$1{,}958{,}688\ \text{per year}$$

Ammonia (NH_3 or NH_4OH) option: very reactive and soluble; also purchased as aqua ammonia:

$$9625\ \text{tons acidity/yr} \times 0.34\ \text{(conversion factor)}$$
$$\times\ \$1000/\text{ton} = \$3{,}272{,}500\ \text{per year}$$

P27.12. For the Stinky Creek coal mine described in Problem P27.10, assuming 3500 gal/min, how

many gallons will be processed every day, every 30 days, and for one year?

Answer:

Per day: 3500 gal/min×60 min/h×24 hr/day = 5,040,000 gal/day

Per 30 days: 5,040,000 gal/day×30 days = 151,200,000 gal/30 days

Per year: 5,040,000 gal/day×365 days/yr = 1,839,600,000 gal/yr

Passive Treatment Design for Acid Drainage for Coal Mines

Passive acid mine drainage requires design and planning. Following are examples of passive treatment calculation problems associated with coal mines. Figure 27.2 provides an overview of various passive acid mine drainage treatment systems.

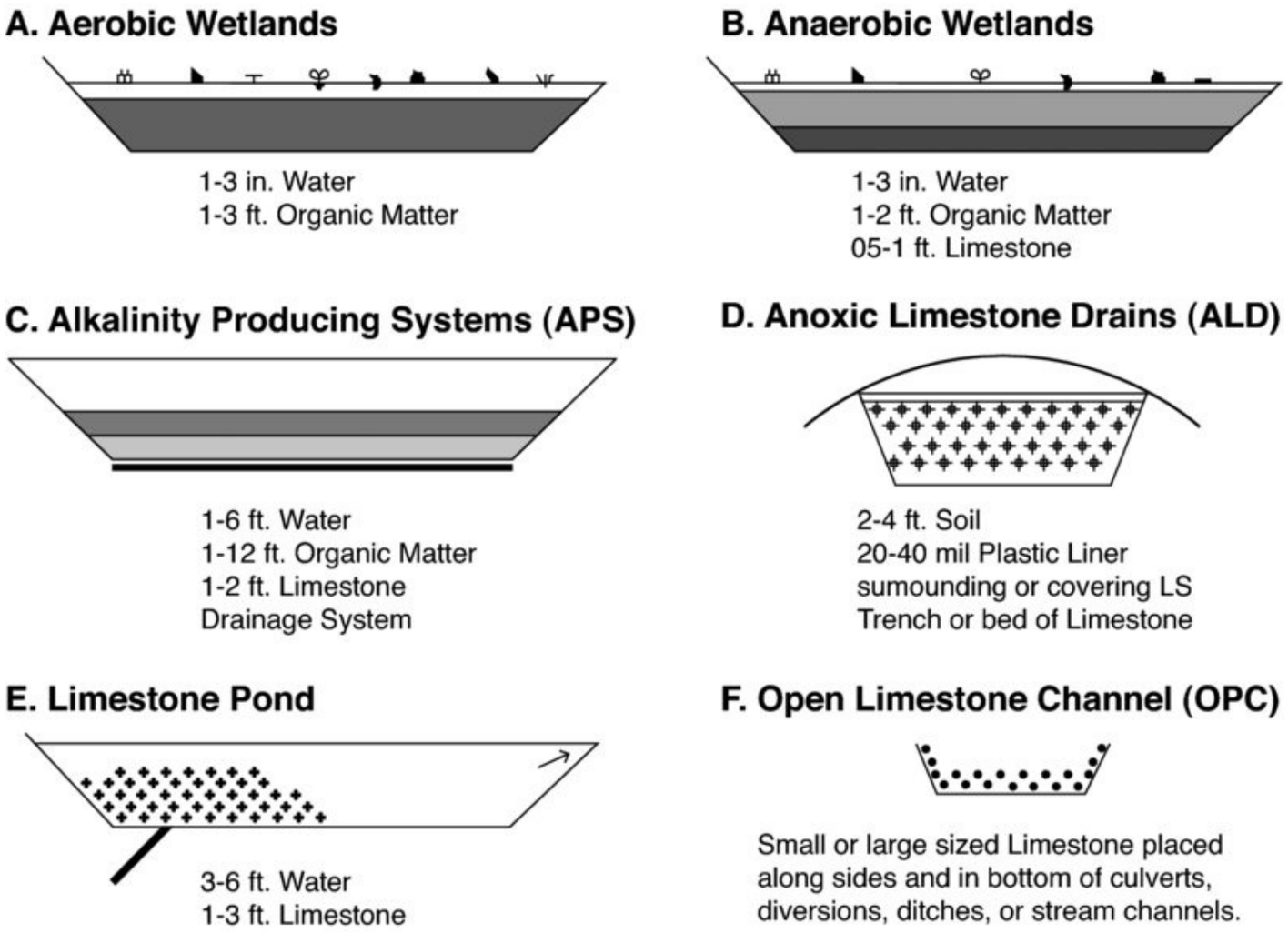


Figure 27.2 Various passive treatment systems to treat AMD. (From Skousen et al., 2000.)

P27.13. A passive treatment system design is needed to address acid drainage coming from the abandoned open-pit Sewickley coal mine in southwestern Pennsylvania. The mine has a consistent 5 ft of water at the bottom of the pit at all times throughout the hydrologic cycle. The flow (60 gal/min) is from the low-end of the pit, which empties into a nearby stream. The area adjacent to the open pit has just enough flat land to consider a passive AMD treatment system option. Water flow and chemistry are as follows:

Flow:	60 gal/min
Acidity:	400 mg/L
pH:	3.3
Iron:	60 mg/L, primarily ferrous
Manganese:	15 mg/L
Aluminum:	35 mg/L
Dissolved oxygen:	2 mg/L
Excavation costs:	\$3000 pit excavation for 250 yd^3
Limestone costs:	\$15/ton
Supplies including plastic wrap:	\$300
Pipes:	\$180

Engineering design and supervision are not included. The water from the pit is directed into an anoxic limestone drain.

a. Determine the tons of acid per year and an ALD design and cost.

   Answer: Tons of acid generated per year: 60 gal/min × 400 mg/L × 0.0022 = 53 tons acid/yr.

b. Determine the ALD treatment size in cubic yards and cubic feet.

   Answer: ALD design and cost: The ALD will be designed for a 10-year life span = approximately 500 tons in ALD. All aluminum and some of the iron (2 mg/L DO) will be expected to precipitate inside the ALD. The ALD size should be based on 125 lb/ft^3 or about 2 tons of limestone per cubic yard.

   ALD treatment volume required:

$$500 \text{ tons} \times 1 \text{ yd}^3/2 \text{ tons of limestone} = 250 \text{ yd}^3 \text{ ALD size}$$

$$250 \text{ yd}^3 \times 27 \text{ ft}^3/\text{yd}^3 = 6912 \text{ ft}^3$$

c. Determine the approximate dimensions of the ALD for a square ALD (option 1) and a rectangular ALD (option 2), with a length-to-width ratio of 2, assuming a uniform depth of 3 ft.

   Answer: The ALD size is 6,912 ft^3 with a uniform depth of 3 ft = 2304 ft^2 surface area.

   Option 1 ALD design: For an ALD with a square shape with a uniform 3 ft depth, take the square root of 2304 ft^2 = 48 linear ft on each side.

   Option 2 ALD design: For an ALD with a rectangular shape with a length-to-width ratio of 2 with a uniform 3 ft depth and a total surface area of 2304 ft^2: area = 2 × 2; x = square root of the area/2; x = 33.941 ft; 2x = 67.882 ft.

d. Determine the cost of the project, assuming that engineering design and field supervision are not included in the bid.

   Answer: Cost estimate: Excavation and field labor costs for the 250 yd^3 ALD pit \$3000. Cost of limestone: \$15 per ton of limestone delivered × 500 tons = \$7500; supplies including plastic to

wrap limestone and other pipes = $300. Pipes = $180. Total cost = $10,980.

P27.14. Acid drainage from the open-pit mine described in Problem 27.13 is piped directly into an anaerobic wetland. The wetland size is based on 10 g of iron removal per square yard of wetland surface area per day. Total iron, Fe(II) and Fe(III), can be measured in the field using colorimetric iron kits, or water samples can be sent to a fixed laboratory for analysis. Site-specific iron removal rates can be determined experimentally in the laboratory using iron removal column testing.

First, find the amount of grams of iron per day in the acid drainage.

$$60\ \text{gal/min} \times 60\ \text{mg/L} \times 3.78\ \text{L/gal} \times 60\ \text{min/hr} \times 24\ \text{hr/day} \times 1\ \text{g/1000 mg} = 19{,}600\ \text{g iron/day}$$

Second, determine the size of the surface area of the wetland needed to treat the soluble iron. Given: 19,600 g iron/day treatment requirement; iron removal rate of 10 g Fe/yd^2.

Minimum wetland design based on iron removal rate: The minimum size of the wetland would be 19,600 g iron/day × 1 yd^2/10 g Fe = 1960 yd^2 or about 2000 yd^2 in wetland surface area to treat the iron in solution in the acid drainage. Assuming a depth of about 4 ft (1.3 yd deep), a square surface area design would be 2000 yd^2 = 1.3 yd × X^2. Each side (X) is 45 yd or 135 ft long, so the minimum area = $L \times W \times D$; = 72,900 ft^3.

The final design with about 60% excess capacity (1.6 times the minimum wetland capacity (72,900 ft^3) increases the final wetland volume, rounded up, to 116,640 ft^3 or about 171 ft by 171 ft × 4 ft deep (57 yd × 57 yd × 1.3 yd deep). If more room is available, it should be built larger, due to the low pH. One foot (0.33 yd) of limestone in the bottom and 2 ft (0.67 yd) of organic material on the top is needed to fill the wetland.

Estimated field installation costs, excluding engineering design and supervision: Excavation and field laborers cost will be about $5000. Organic material is 57 yd × 57 yd × 0.67 yd = 2177 yd^3 at $25/$yd^3$ = $54,425. Limestone at 57 yd × 57 yd × 0.33 yd thickness = 1072 yd^3 × 2 tons limestone/yd = 2144 tons of limestone at $15/ton = $32,150.

Total cost = $86,585. What are the chemical treatment costs per year using sodium hydroxide (option 1) or ammonia (option 2)? Assume 53 tons/yr of acid neutralization requirement based on the acid drainage conditions.

Answer:

Option 1: sodium hydroxide (NaOH, conversion factor (cf) of 784 for 20% concentration at $0.95/gal): 53 tons/yr × 784 ft^3 × $0.95/gal = $39,474

Option 2: ammonia (NH_3, cf of 0.34 and $1000/ton): 53 tons/yr × 0.34 ft^3 × $1000/ton = $18,020.

Passive Acid Drainage Treatment Example

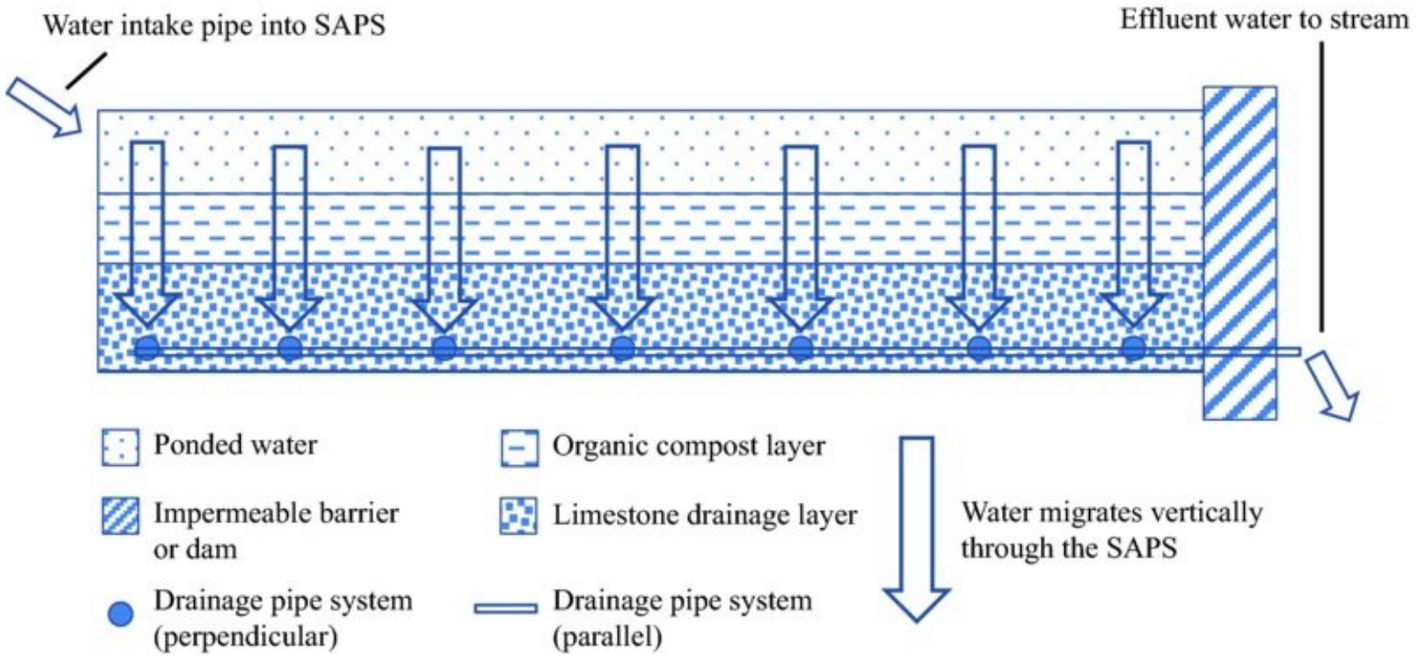


Figure 27.3 SAPS cross section (From Frippl et al., 2000.)

P27.15. In this set of calculations, the dissolved oxygen (DO) and pH are evaluated for passively treating acid drainage using a SAPS design (Fripp et al., 2000, see Figure 27.3). Many of the calculations required are also applicable in part for other treatment design. Given:

Life of project:	20 years
$CaCO_3$ content of limestone:	90%
Dissolution of limestone:	75%
Bulk density (r):	100 lb/ft^3
Residence time (T_d):	15 h
V_v:	40%

From sampling data:

$$Q = \text{total flow} = 11.5 \text{ gal/min} \times 3.78 \text{ L/gal}$$
$$= 43.53 \text{ L/min}$$

Weighted average of acidity:	200 ppm
Weighted average Fe:	1.0 ppm
Weighted average Al:	10.3 ppm
Weighted average Mn:	26.4 ppm
pH:	3.3 to 3.8
DO:	7 ppm
Maximum sulfate:	850 ppm

Evaluation of Acidity Data in Passive Acid Drainage Treatment Example

In this SAP example, the DO is too high for an anoxic limestone drain (ALD) and the pH is too low for a treatment wetland. Soluble metal concentrations in the acid drainage are too high for an oxic limestone drain (OLD). An OLD resembles an ALD that has provisions for periodic flushing of the sludge at the bottom of the treatment unit. OLDs are not well suited for acid drainage with highly soluble iron concentrations, which would rapidly precipitate out in the high dissolved oxygen environment, filling up the OLD with iron-rich sludge. For this example it is assumed that site conditions do not permit capping, sealing, or grout injection. It is also assumed that a major environmental goal is to reduce the metal precipitation in streams. Therefore, of the choices available for a passive acid drainage treatment system, a SAPS is the remedial option selected.

Limestone requirements: The calculation for limestone is the same as for an ALD.

$$M = f(Q, \text{life}, \ \text{CaCO}_3 \text{ content of limestone}, \ \text{dissolution}, \ \text{residence time})$$

$$M = \frac{Q \times \rho \times T_d}{V_v} + \frac{Q \times \text{alkalinity added} \times \text{life}}{\text{CaCO}_3 \text{ content}}$$

Acidity < 300 ppm; need one SAP cell to add 200 mg/L alkalinity. M = 260 mt = 300 tons (rounded up). Volume = 6000 ft^3. SAP configuration: 5- to 6-ft-deep pool over organic matter 2 ft in depth, which is interred over a bed of 2-ft-deep limestone. The minimum length-to-width ratio should be 2.

The limestone pieces should have a minimum size of no. 4 (nominal minimum ¾-in. diameter; nominal maximum 1- to 1½-inch diameter; a typical use for the no. 4 size is as road base). Can be as large as 2-in. diameter. The limestone requires a minimum of 90% $CaCO_3$ and a maximum of 5% Mg_2CO_3. Typical organic material should be spent mushroom compost with a minimum 10% $CaCO_3$ content.

Settling Pond Requirements

A settling pond is required to store the sludge that will be produced during passive treatment of the acidic groundwater. The calculations are the same as those required to size any settling pond.

$$\text{Iron: } Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
$$56 \text{ g/g mole} \rightarrow 107 \text{ g/gmol}$$

$$\text{Manganese: } Mn^{2+} + 2H_2O \rightarrow Mn(OH)_2 + 2H^+$$
$$55 \text{ g/g mol} \rightarrow 89 \text{ g/g mol}$$

$$\text{Aluminum: } Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$
$$55 \text{ g/g mol} \rightarrow 89 \text{ g/g mol}$$

Iron Sludge Production

Inflow iron: 1.0 mg/L × 43.53 L/min × (1/1000) g/mg × (1/1000) kg/g × 2.205 lb/kg × 60 min/h × 24 h/day = 0.138 lb/day. Inflow Fe sludge = 0.138 lb/day × 107/56 = 0.264 lb/day. It can be assumed that the weight of sludge is equivalent to that of water: r_w = 62.4 lb/ft^3. Therefore, the inflow of the iron sludge volume per day = 0.264 lb/day × (1/62.4) lb/ft^3 = 0.00423 ft^3/day.

Similarly:

Inflow manganese sludge: 0.09463 ft^3/day

Inflow aluminum sludge: 0.06593481 ft^3/day

Total sludge: 0.1648 ft^3/day

Volume of sludge (20 years): 20 years×365 days/yr×0.1648 ft^3/day = 1200 ft^3

Assume a 24-h detention time:

$$\begin{aligned} \text{volume} &= 11.5 \text{ gpm} \times (1/7.48)\ ft^3/\text{gal} \\ &\quad \times 60 \text{ min/h} \times 24 \text{ h} = 2213\ ft^3 \\ \text{total volume} &= 3413\ ft^3 \rightarrow 3500\ ft^3 \text{(rounded up)} \end{aligned}$$

The detention pond should be 4 ft deep with a minimum length-to-width ratio of 3.

Acid Drainage Calculations

Acidity is a measure of the amount of base needed to neutralize a volume of water. The unit for acidity can be mol/L or mg/L as $CaCO_3$. Our calculations will result in values of acidity in units of mg/L as $CaCO_3$. In acid mine drainage, acidity values can vary from 50 mg/L to 10,000 mg/L as $CaCO_3$.

In uncontaminated water or water polluted by "acid rain," water pH may be 3.5 to 4.5, but very little mineral acidity is present in the water. The acidity in West Virginia streams due to acid rain usually varies between 25 and 100 mg/L as $CaCO_3$. However, for acid mine drainage, the acidity in water includes hydrogen-ion acidity (low pH) and, more important, mineral acidity. Mineral acidity arises from the presence of dissolved metals (e.g., iron, aluminum, and manganese) in the water. In drainage from other types of surface or deep mining (metal mines), the water may contain significant amounts of zinc, copper, nickel, lead, and so on, which also add mineral acidity. However, when dealing with AMD from coal mines in the eastern United States, the use of pH, iron, aluminum, and manganese usually accounts for the majority of the acidity.

As an example, the acidity of coal mine drainage can be estimated, where calculated acidity is expressed as mg/L $CaCO_3$ equivalent, all metal concentrations are in mg/L, and 50 mmol/L of acidity is converted into mg/L $CaCO_3$ equivalent. For acid mine drainage with a pH below 4.5 (no alkalinity present), the acidity calculation predicts the laboratory-measured acidity of the water relatively accurately.

Acidity Equations

$$\begin{aligned} \text{Calculated acidity} &= 50(2Fe^{2+}/56 + 3Fe^{3+}/56 \\ &\quad + 3Al^{3+}/27 + 2Mn^{2+}/55 + 1000(10^{-pH})) \\ \text{Percent difference of acidity} &= [(\text{measured acidity} - \\ &\quad \text{calculated acidity})/\text{measured acidity}] \times 100 \end{aligned}$$

Flow Measurement Calculations

The Patton shaft and the Patton borehole release acid drainage into the Ten Mile Creek near East Loyalhanna, Pennsylvania. The acid drainage from the shaft is not measurable because it comes into the bottom of a pond, and the amount of acid drainage from the shaft can only be determined from the outflow of water from the pond minus the inflow into the pond. The flow from the Patton borehole can be

measured in a channel a few feet from the borehole. You must determine the acid drainage flow coming from both the shaft and the borehole. Cross sections of incoming streams to the pond and outgoing streams from the pond were measured for width, depth, and velocity. From the difference between inflowing and outgoing water, the shaft flow can be estimated. Convert all flows to gallons per minute.

P27.16. What is the water flow in each of the tributaries?

Answer: The data are provided in Table 27.2.

$$\begin{aligned}&\text{Small tributaries} = (\times 3) = 0.525\ \text{ft}^3/\text{s}\\ &\quad \text{or } 235.7\ \text{gal/min}\\ &\text{Big tributary} = 1.075\ \text{ft}^3/\text{s or } 482.7\ \text{gal/min}\\ &\text{Total Upstream} = 1.6\ \text{ft}^3/\text{s or } 718.4\ \text{gal/min}\end{aligned}$$

P27.17. What is the flow of water coming out of the shaft?

Answer: The data are provided in Table 27.3.

$$\begin{aligned}\text{Total shaft flow} &= \text{downstream } (\text{ft}^3/\text{s})\\ &\quad - \text{upstream } (\text{ft}^3/\text{s})\\ &= 5.39\ \text{ft}^3/\text{s} - 1.60\ \text{ft}^3/\text{s}\\ &= 3.79\ \text{ft}^3/\text{s or } 1,701.6\ \text{gal/min}\end{aligned}$$

P27.18. What is the flow of water coming from the borehole?

Answer: See Table 27.3.

$$\text{Borehole Flow} = 2.72\ \text{ft}^3/\text{s or } 1221\ \text{gal/min}$$

P27.19. What is the flow of water coming from the shaft and the borehole?

Answer: See Table 27.3.

$$\begin{aligned}&\text{Total shaft and borehole flow}\\ &= 3.79\text{ft}^3/\text{s} + 2.72\text{ft}^3/\text{s}\\ &= 6.51\text{ft}^3/\text{s or } 2923\ \text{gal/min}\end{aligned}$$

Table 27.2 Data for Problem P27.16.

	Composition of AMD (mg/L)							Acidity (mg/L as $CaCO_3$)		
pH	**Fe^{2+}**	**Fe^{3+}**	**Al^{3+}**	**Mn^{2+}**	**Zn^{2+}**	**Cu^{2+}**	**Ni^{3+}**	**Measured**	**Calculated**	**Difference[a] (%)**
3.9	98	1	0	0	0	0	0	184	184	0
3.9	0	0	106	0	0	0	0	578	595	−2.9
3.6	0	0	0	97	0	0	0	186	189	−1.6
3.8	13	0	47	42	0	0	0	335	369	−10
3.4	0	4	4	1	0	0	0	65	55	+15.8
2.8	0	16	21	4	0	0	0	203	246	−21.2
3.7	9	15	31	6	2	0	0	295	252	+14.4
3.1	14	33	47	9	2	1	1	408	439	−7.5
3.6	4	337	80	4	1[b]	0	1[b]	1,263	1,378	−9.1
3.0	870	259	118	7	15	0	4	3,152	2,999	+4.9
3.6	10	22	41	20	1	0	1	516	358	+30.6
4.3	151	55	38	42	2	0	2	1,212	715	+41
2.2	110	440	140	76	60	92[b]	2	2,750	2,847	−3.5
3.0	121	955	118	7	0	0	0	4,720	3,492	+26
3.8	19	170	100	28	40	140	5	1,820	1,397	+23.3
2.7	3500	1900	48	65	8	24	4	14,400	11,883	+17.5

[a] $\frac{\text{Measured} - \text{calculated}}{\text{measured acidity}} \times 100 =$ (carry the + or − sign).

[b] Use $2Zn^{2+}/65$, $2Cu^{2+}/64$, $3Ni^{3+}/59$.

Table 27.3 Data for Problems P27.17 to P27.19

Station	**Width (ft)**	**Depth (ft) (ft^3/s)**	**Velocity (ft/s) = gal/min**	**Flow (ft^3/s and gal/min)**
Upstream: Three Small Tributaries with About the Same Dimensions				
6 in.	1.0	0.5	0.35	× 3 = 0.525 ft^3/s or 235.7 gal/min
Total width: 1 ft each				
Upstream: Big Tributary				
6 in.	1.0	1.45	0.5	0.725 ft^3/s
1.5 ft	1.0	0.35	0.3	0.105 ft^3/s
2.5 ft	1.0	1.25	0.1	0.125 ft^3/s
3.5 ft	1.0	1.20	0.1	0.120 ft^3/s
Total width: 4.0 ft				1.075 ft^3/s or 482.7 gal/min
			Upstream Total Flow =	1.6 ft^3/s or 718.4 gal/min
Downstream: Left Fork				

6 in.	1.0	0.3	0.6	0.18 ft^3/s
1.5 ft	1.0	0.6	1.3	0.78 ft^3/s
2.5 ft	1.0	0.5	1.1	0.55 ft^3/s
3.5 ft	1.5	0.4	0.9	0.54 ft^3/s
5.0 ft	1.0	0.25	0.8	0.20 ft^3/s
Total width: 5.5 ft				2.25 ft^3/s or 1010 gal/min
Downstream: Right Fork				
6 in.	1.0	0.2	0.5	0.10 ft^3/s
1.5 ft	1.0	0.3	1.4	0.42 ft^3/s
2.5 ft	1.0	0.65	1.95	1.27 ft^3/s
3.5 ft	1.0	0.75	1.80	1.35 ft^3/s
Total width: 4.0 ft				3.14 ft^3/s or 1410 gal/min
			Downstream Total Flow =	5.39 ft^3/s or 2420 gal/min
Downstream − upstream = total shaft flow = 5.39 ft^3/s − 1.60 ft^3/s = 3.79 ft^3/s or 1701.6 gal/min				
Borehole Flow (Channel Dimentions)				
2 ft width	0.8 ft depth	1.7 ft/s velocity	Borehole flow = 2.72 ft^3/s or 1221 gal/min	
Total shaft and borehole flow = 3.79 ft^3/s + 2.72 ft^3/s = 6.51 ft^3/s or 2923 gal/min				

Estimating Flows from Pipes

The overall water balance problem is to determine the total amount of acid drainage going into a wetland. Acid drainage is introduced into a wetland from a treatment system through two pipes, a 6-in.-diameter pipe and a 4-in.-diameter pipe. A weir is at the end of the remediation system. Remember, first to calculate the cross section of the pipe in square ft (πr^2), then multiply by velocity (ft/s) to get flow rate in ft^3/s or gal/min. This is the amount of water going into the wetland: flow rate (gal/min or ft^3/s) = cross-sectional area of the pipe (ft^2) × velocity (ft/s)

P27.20. A 6-in. diameter pipe is full and conveys water at a velocity of 2.1 ft/s.

Answer:

$$\begin{aligned} 6 \text{ in.} \times 12 \text{ ft/in.} &= 0.25 \text{ ft radius} \\ 3.15 \times 0.25^2 &= 0.196 \text{ ft}^2 \times 2.1 \text{ ft/s} \\ &= 0.4116 \text{ ft}^3/\text{s or } 184.8 \text{ gal/min} \end{aligned}$$

P27.21. A 4-in.-diameter pipe is full and conveys water at a velocity of 0.475 ft/s.

Answer:

$$4 \text{ in.} \times 12 \text{ ft/in.} = 0.1667 \text{ ft radius}$$
$$3.15 \times 0.1667^2 = 0.0876 \text{ ft}^2 \times 0.475 \text{ ft/s}$$
$$= 0.04145 \text{ ft}^3/\text{s or} 18.6 \text{ gal/min}$$

P27.22. What is the total flow into the wetland in gal/min of both pipes (in Problems P27.20 and P27.21)?

Answer: Total flow with both 6-in.- and 4-in.-diameter pipes into the wetland is 184.8 gal/min + 18.6 gal/min = 203.4 gal/min for both pipes.

Estimating Flows from Weirs

P27.23. Calculate the amount of water flowing out of the wetland. One way to measure water flow without a field meter is to use a weir with standard dimensions. The water flowing across a weir is based on the dimensions of the weir and the velocity of water. The rectangular weir at the end of the wetland is 12 in. (1 ft) across, and the height of water is 2.85 in. (0.2375 ft). The velocity is 1.45 ft/s. What is the total flow in gal/min of the treated water out of the wetland?

Answer: 1 ft × 0.2375 ft × 1.45 ft/s = 0.344375 ft^3/s or 154.6 gal/min.

P27.24. How much water in gal/min is being lost in the wetland?

Answer: Water lost in the wetland = flow into wetland – flow out of wetland 203.4 − 154.6 = 48.8 gal/min.

P27.25. What amount of water is flowing through the following pipes and weirs?

a. A 4-in.-diameter pipe (completely filled) at a velocity of 1.2 ft/s.

   Answer: 47 gal/min.

b. An 18-in.-diameter pipe at a velocity of 1.5 ft/s.

   Answer: 1190 gal/min.

c. A weir 3 ft across with water 24 in. deep flowing at 1.25 ft/s.

   Answer: 3367.5 gal/min.

d. A weir 5 ft across with water 36 in. deep flowing at 2.00 ft/s.

   Answer: 13,470 gal/min.

P27.26. What is the acidity of water (mg/L) that has the following characteristics?

	pH	**Fe^{2+}**	**Fe^{3+}**	**Al^{3+}**	**Mn^{2+}**	**Acidity (mg/L)**
Sample 1	3.6	25	53	35	10	412
Sample 2	3.2	148	22	95	40	955
Sample 3	2.7	120	433	155	85	2490

Answer: Use the following equation to calculate acidity in mg/L.

$$\text{Calculated acidity} = 50\,(2Fe^{2+}/56 + 3Fe^{3+}/56 + 3Al^{3+}/27 + 2Mn^{2+}/55 + 1000\,(10^{-pH}))$$

Sample 1 = 412 mg/L;
sample 2 = 955 mg/L;
sample 3 = 2490 mg/L.

P27.27. For practice with acid drainage calculations, evaluate the acid load for the following combinations. The flows and acidity are based on earlier problems. Use a conversion factor of = 0.0022 to convert mg/L into tons/yr alkalinity.

a. Given: sample 1: acidity = 412 mg/L; 4-in.-diameter pipe (filled completely) at a velocity of 1.2 ft/s = 47 gal/min.

   Answer: 47 gal/min×412 mg/L×0.0022 cf = 42.6 tons/yr.

b. Given: sample 3: acidity = 2490 mg/L; 4-in.-diameter pipe (filled completely) at a velocity of 1.2 ft/s = 47 gal/min.

   Answer: 47 gal/min×2490 mg/L×0.0022 cf = 257.5 tons/yr.

c. Given: sample 2: acidity = 955 mg/L; 18-in.-diameter pipe (filled completely) at a velocity of 1.5 ft/s = 1190 gal/min.

   Answer: 1190 gal/min×955 mg/L×0.0022 = 2502.8 tons/yr.

d. Given: sample 2: acidity = 955 mg/L; water pouring through a weir 3 ft across with water 24 in. deep flowing at 1.25 ft/s = 3367.5 gal/min.

   Answer: 3367.5 gal/min×955 mg/L×0.0022 = 7,083.6 tons/yr.

e. Given: sample 3: acidity = 2490 mg/L; water pouring through a weir 3 ft across with water 24 in. deep flowing at 1.25 ft/s = 3367.5 gal/min.

   Answer: 3367.5 gal/min × 2490 mg/L × 0.0022 = 18,499.9 tons of acid/yr.

P27.28. The best chemical for treating AMD is usually the one that is the lowest cost for a specified acid load (unless there is some overarching reason why the lowest-cost chemical may not work in that circumstance). The conversion factors and prices for each chemical are provided in Table 27.4.

Calculate each chemical reagent cost for acid loads of three cases: case 1, 43 tons/yr; case 2, 7084 tons/yr; case 3, 18,500 tons/yr. What would be the chemical of choice in each situation based on chemical costs alone?

Answer: See Table 27.5.

Case 1; $Ca(OH)_2$ is the lowest-cost treatment compound, at $4773.

Case 2; $Ca(OH)_2$ is the lowest-cost treatment compound, at $786,324.

Case 3; $Ca(OH)_2$ is the lowest-cost treatment compound, at $2,047,950.

Table 27.4 Selected Chemical Compounds Used in Acid Drainage Treatment (2013 Costs)

			Conversion	Neutralization	
Common Name	**Chemical Name**	**Formula**	**Factor[a]**	**Efficiency[b]**	**Bulk Cost**
Limestone	Calcium carbonate	$CaCO_3$	1.00	30%	$15/ton
Hydrated lime	Calcium hydroxide	$Ca(OH)_2$	0.74	90%	$120/ton
Soda ash	Sodium carbonate	Na_2CO_3	1.06	60%	$900/ton ($0.44/lb)
20% liquid caustic	Sodium hydroxide	NaOH	784	100%	$0.95/gal
50% liquid caustic	Sodium hydroxide	NaOH	256	100%	$3.25/gal
Ammonia	Anhydrous ammonia	NH_3	0.34	100%	$680

[a]The conversion factor may be multiplied by the estimated tons acid/yr to get the tons of chemical needed for neutralization per year. For liquid caustic the conversion factor gives gallons needed for neutralization.

[b]The neutralization efficiency estimates the relative effectiveness of the chemical in neutralizing AMD acidity. For example, if 100 tons of acid/yr was the amount of acid to be neutralized, it can be estimated that 82 tons of hydrated lime would be needed to neutralize the acidity in the water [100(0.74)/0.90].

[c]The price of the chemical depends on the quantity being delivered. “Bulk” means delivery of chemical in a large truck. Liquid caustic prices are for gallons; others are in tons. Significant shifts in prices (usually, increases) occur for many of these compounds, and variations exist based on volume ordered and location.

Table 27.5

	Acid Load		
Chemical	**43 tons/yr**	**7084 tons/yr**	**18,500 tons/yr**
$NaCO_3$	$45,580	$7,509,040	$19,557,000
NaOH 20%	$75,852	$12,496,176	$32,545,800
NaOH 50%	$46,784	$7,707,392	$20,073,600
NH_3	$16,082	$2,649,416	$6,900,300
$Ca(OH)_2$	$4,773	$786,324	$2,047,950

References and Suggested Reading

Brady, K.B.C., and Hornberger, R.J., 1990. The prediction of mine drainage quality in Pennsylvania. Water Pollution Control Association of Pennsylvania Magazine, vol. 23, no. 5, pp. 8–15.

Brady, K.B.C., Perry, E.F., Beam, R. L., Bisko, D.C., Gardner, M.D., and Tarantino, J.M., 1994. Evaluation of acid–base accounting to predict the quality of drainage at surface coal mines in Pennsylvania, USA. In: Proceedings of the International Land Reclamation and Mine Drainage Conference and the 3rd International Conference on the Abatement of Acidic Drainage. Special Publication SP 06A-94. U.S. Department of the Interior, Bureau of Mines, Washington, DG, pp. 138–147.

diPretoro, R.S., 1986. Premining Prediction of Acid Drainage Potential for Surface Coal Mines in Northern West Virginia. M.S. thesis., Geology Department, West Virginia University, Morgantown, WV, 217 p.

diPretoro, R.S., and Rauch, H.W., 1988. Use of acid–base accounts in premining prediction of acid drainage potential: a new approach from northern West Virginia. In: Mine Drainage and Surface Mine Reclamation, vol. 1, Mine Water and Mine Waste. Information Circular 9183. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 1–10.

Evangelou, V.P., 1998. Environmental Soil and Water Chemistry: Principles and Applications. Wiley, New York, 564 pp.

Fripp, J., Ziemkiewicz, P.F., and Charkavorki, H., 2000. Acid Mine Drainage Treatment. Publication ERDC TN-EMRRP-SR-14. EMRRP, U.S. Army Corps of Engineers, Washington, DC, 7 pp.

Perry, E., 1998. Interpretation of acid–base accounting. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, K.B.C. Brady, T. Kania, M.W. Smith and R.J. Honberger, eds. Department of Environmental Protection, Harrisburg, PA.

Perry, E., and Brady, K., 1995. Influence of neutralization potential on surface mine drainage quality in Pennsylvania. In: Proceedings of the 16th West Virginia Surface Mine Drainage Task Force Symposium, April 4–5, West Virginia University, Morgantown, WV.

Plummer, L.N., Wigley, T.M.L., and Parkhurst, D.L., 1978. Kinetics of calcite dissolution in CO_2–water systems at 5-degrees-C to 60-degrees-C and 0.0 to 1.0 atm CO_2. American Journal of Science, vol. 278, pp. 179–216.

Singer, P.C. and Stumm, W., 1970. Acidic mine drainage: the rate-determining step. Science, vol. 167, pp. 1121–1123.

Skousen, J.G., Smith, R.M., and Sencindiver, J.C., 1990. The development of the acid base account. Green Lands, vol. 20, no. 1. West Virginia Mining and Reclamation Association, Charleston, WV, pp. 32–37.

Skousen, J., Sexstone, A., and Ziemkiewicz, P.F., 2000. Acid Mine Drainage Control and Treatment. American Society of Agronomy–Crop Science Society of America–Soil Science Society of America, Madison, WI, pp. 131–168.

Smith, M.W., and Brady, K.B.C., 1998, Alkaline addition. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, K.B.C. Brady, T. Kania, M.W. Smith, and R.J. Hornberger, eds. Department of Environmental Protection, Harrisburg, PA, pp. 5–1 to 5–9.

Smith, R.M., and Sobek, A.A., 1978. Physical and chemical properties of overburdens, spoils, wastes and new soils. In: Reclamation of Drastically Disturbed Lands, F.W. Schaller and P. Sutton, eds. American Society of Agronomy, Madison, WI, pp. 149–172.

Sobek, A.A., 1987. The use of surfactants to prevent AMD in coal refuse and base metal tailings. In: Proceedings of an Acid Mine Drainage Seminar/Workshop, Environment Canada, Halifax, NS, Canada, March 23–26, pp. 357–391.

Sobek, A.A., Schuller, W.A., Freeman, J.R., and Smith, R.M., 1978. Field and Laboratory Methods Applicable to Overburden and Minesoils. EPA 600/2-78-054. U.S. Enviornmental Protection Agency, Washington, DC 203 pp.

Sobek, A.A., Skousen, J.G., and Fisher, S.E., Jr., 2000. Chemical and physical properties of overburdens

and minesoils. In: Reclamation of Drastically Disturbed Lands. Agronomy No. 41. American Society of Agronomy, Madison, WI, pp. 77–104.

Strock, N., 1998. Reclamation and revegetation. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, K.B.C. Brady, T. Kania, M.W. Smith, and R.J. Hornberger, eds. Department of Environmental Protection, Harrisburg, PA, pp. 12–1 to 12–5.

Tarrantino, J.M., and Shaffer, D.J., 1998. Planning the overburden analysis. Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, K.B.C. Brady, T. Kania, M.W. Smith, and R.J. Hornberger, eds. Department of Environmental Protection, Harrisburg, PA, pp. 13–1 to 13–13.

U.S. Environmental Protection Agency, 1981. U.S. EPA Chart Comparing Sulfide and Hydroxide Solubilities. EPA-600/2-82-OIIC. U.S. EPA, Washington, DC.

28
Mine Reclamation Policy and Regulations of Selected Jurisdictions

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This chapter provides an overview of selected acid mine drainage (AMD) policies and regulations from a variety of sources. The federal laws and policies regarding acid mine drainage in the United States are examined, followed by selected state laws. Selected international policies and regulations for acid mine drainage are reviewed for countries on different continents with long histories of mining and acid mine drainage: Australia, Canada, Germany, and South Africa.

Background

Environmental impacts, notably water pollution, from coal and gold mining are well documented. The majority of the cases in the literature represent acid rock drainage (ARD) or mine drainage from abandoned mine sites, and result from either point sources or non-point sources. Laws and regulations leading up to the programs currently in place and summarized below resulted from two distinct mining industries: the coal-mining industry and the gold-mining industry.

Coal has been mined in the United States since the 1740s. With widespread strip mining, by the 1930s environmental concerns were being raised, and state enacting laws to regulate the coal-mining industry began in West Virginia (1939), followed by Indiana (1941), Illinois (1943), and Pennsylvania (1945). With the great demand for coal during World War II, environmental concerns related to coal mining were set aside until after the war, when states began to enact and expand their respective regulatory programs. Some of these state programs required mining permits and posting of bonds to ensure reclamation after mining was complete. Surface mining of coal became increasingly popular, making up 33% of the total production of coal in 1963, and increasing to 60% by 1973.

President Ford vetoed mining regulation bills in 1974 and 1975, an action that reflected concern over the potential adverse impact on the coal industry, increased inflation, and the possibly of adding to a restrictive energy supply. However, President Carter campaigned in Appalachia in 1976 and promised to sign the bills, and he signed the Surface Mining Control and Reclamation Act of 1977 (SMCRA) into law on August 3, 1977. When it passed SMCRA, Congress required that coal mines be reclaimed and backfilled as a routine element of reclamation. The concept had not generally been applied to noncoal surface mines. Large open-pit metallic mines were not common in California and elsewhere throughout the western states until the discovery of large disseminated gold deposits (Testa and Pompy, 2007). The Carlin mine was discovered in 1961 in northern Nevada. Carlin became the first large gold mine on what is now known as the Carlin Trend. Carlin-type deposits are characterized by extremely fine-grained gold that cannot be seen by the human eye or concentrated by panning. By 1970 another other mine, the Cortez operation, had been found and developed in northern Nevada. Then came the discovery of the Pinson, Preble, Sterling, and Dee mines and development of the Getchell Trend, second only to the Carlin Trend in Nevada gold production. These successes and higher gold prices fueled a Nevada exploration boom during the 1980s. The gold rush spread quickly to California.

Cyanide heap leaching technology made it possible for very large low-grade deposits to be mined

economically. Low-grade deposits that could not be mined economically by underground or open-pit methods, especially when using more costly vat leaching processes, were suddenly sought out. Numerous large open-pit mines began to spring up along the gold-bearing trends in Nevada and California.

Most regulatory frameworks for open-pit mining were adopted prior to the discovery of the large disseminated gold deposits and proliferation of large open-pit gold heap leach operations. The surge in large open-pit metallic mines was not anticipated when California's Surface Mining and Reclamation Act was adopted in 1975. As more and more large new open-pit mining operations sprang up, there was renewed interest in mine reclamation.

In this chapter we summarize significant federal, state, and international laws and regulations pertaining to environmental effects of mining, reclamation, and notably, as applicable to AMD and ARD. As with most U.S. legislation and regulation, significant environmental programs are overseen at the federal level, with individual states having the responsibilities and cooperative programs in coordinating and administrating certain elements of the programs. With abandoned mines, the state and tribal authorities taking responsibility for these efforts through an agreement in 1993 to form the National Association of Abandoned Mine Lands Program to coordinate these efforts, share knowledge and foster positive cooperation. Additional programs have been instituted by the U.S. Geological Survey, emphasizing hardrock mining sites at a catchment scale in Colorado and Montana (U.S. Geological Survey, 2007), and the U.S. Bureau of Land Management, which oversees abandoned mines on public land (U.S. Bureau of Land Management, 2008).

Federal Laws and Regulations: United States

Comprehensive Environmental Response, Compensation, and Liability Act, Section 106: Superfund

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as the Superfund, was enacted by Congress on December 11, 1980, with the battle cry "*shovels first—lawyers second*!" This law created a tax on the chemical and petroleum industries and provided broad federal authority to respond directly to releases or threatened releases of hazardous substances that may endanger public health or the environment. In general terms, CERCLA established prohibitions and requirements concerning closed and abandoned hazardous waste sites, provided for the liability of persons responsible for releases of hazardous waste at these sites, and established a trust fund to provide for cleanup when no responsible party could be identified. In the five years following its enactment, $1.6 billion was collected and the tax went to a trust fund for cleaning up abandoned or uncontrolled hazardous waste sites.

CERCLA also enabled revision of the National Contingency Plan (NCP). The NCP provided the guidelines and procedures needed to respond to releases and threatened releases of hazardous substances, pollutants, or contaminants. The NCP also established the National Priority List (NPL).

On October 17, 1986, CERCLA was amended by the enactment of the Superfund Amendments and Reauthorization Act (SARA). This law authorizes two types of response actions:

1. Short-term removals, where actions may be taken to address releases or threatened releases, requiring prompt response
2. Long-term remedial response actions, which permanently and significantly reduce the dangers associated with releases, or threats of releases, of hazardous substances that were serious but not

immediately life threatening. These actions could be conducted only at sites listed on the U.S. Environmental Protection Agency's (EPA's) NPL.

By 1990, 109 (45 mining and 64 mining-related sites) mining and mining-related Superfund sites were listed on the NPL, with more sites anticipated. Cleanup alternatives ranged from “no action,” at little cost, to removal of the entire mineralized zone, costing millions of dollars. As of November 2010, the NPL included 62 proposed sites (5 on federal lands), 1280 final sites (158 on federal lands), and 347 deleted sites (15 on federal lands).

An inventory of abandoned mine lands (AML's) is listed in the Comprehensive Environmental Response, Compensation and Liability Information System (CERCLIS). This system provides a list of mining and mineral processing sites on the NPL or deleted from the NPL, all AML sites from the EPA's database of hazardous waste sites, potential hazardous waste sites, remedial activities nationwide, and AML sites with EPA removals and emergency responses. As of March 2010, the AML CERCLIS inventory included 561 sites, with 108 AML sites listed on the NPL.

From a remediation perspective, CERCLA incorporates two main phases: preremedial and remedial. The preremedial phase incorporates a preliminary assessment, a site investigation, and if appropriate, placement of the site on the NPL. The remedial phase incorporates a remedial investigation, a feasibility study, and a record of decision in the remediation approach.

Resource Conservation and Recovery Act

The Resource Conservation and Recovery Act (RCRA), an amendment to the Solid Waste Disposal Act, was passed in 1976. In 1980, Congress specifically, albeit temporarily, excluded oil and gas wastes, mining wastes, waste from the combination of coal and other fossil fuels, and cement kiln dust waste from being regulated under Subtitle C, Hazardous Waste (Bevill Amendment).

Surface Mining Control and Reclamation Act

The Surface Mining Control and Reclamation Act of 1977 (SMCRA) is the primary federal law that regulates the environmental effects of coal mining in the United States. Pronounced “smack-ra,” this federal program was to provide a regulatory framework for regulating coal mining and providing a mechanism for remediation activities for lands and waters that had been affected adversely by past coal-mining activities. Two programs were created: one for regulating active coal mines and a second for reclaiming abandoned mine lands. SMCRA also created the Office of Surface Mining (OSM), now the Office of Surface Mining Reclamation and Enforcement (OSMRE), located within the Department of the Interior, for the purpose of promulgating regulations, funding state regulatory and reclamation efforts, and ensuring consistency among state regulatory programs.

SMCRA placed a fee of 35 cents per ton of surface-mined coal, 15 cents per ton of coal mined underground, and 10 cents per ton of lignite on all active mining operations. The fees are collected by the OSMRE and put into the Abandoned Mine Land Reclamation Fund. Funds are then transferred to the states based on congressional budgetary appropriations. In general, 50% of the reclamation fees collected in each state is returned to the state for reclamation, provided that the responsible party(ies) have a federally approved reclamation program. The remaining 50% of the SMCRA fee is used by the OSMRE for high-priority projects and other programs.

SMCRA funds are intended for cleanup projects at coal mines that were abandoned prior to August 3, 1977, and cannot be used on sites that are already on the NPL. In some cases, SMCRA can be used to address abandoned hardrock mines provided that the state certifies that the responsible party(ies) have

already addressed all of the coal mine problems under their jurisdiction. To date, the Hopi and Navajo tribes and the states of Louisiana, Montana, Texas, and Wyoming have certified the completion of all coal mine reclamation projects.

Abandoned mines are reclaimed under the National Abandoned Mine Land Program under OSMRE. Funds are raised via a levy on active coal mines and deposited into the AML fund. This fund is a trust administered by the U.S. Treasury to pay for the reclamation of mines abandoned before passage of the SMCRA.

Title 30 of the *Code of Federal Regulations* Part 876

Regulations pertaining to AMD treatment and abatement is found under Title 30 of the *Code of Federal Regulations* Part 876 (30 CFR Part 876), Section 876, Acid Mine Drainage Treatment and Abatement Program. This set of federal regulations provides scope, information collection, eligibility, treatment and abatement plan content, and plan approval. Applicable to any state or Indian tribe having an approved abandoned mine land program, such a tribe may receive grant monies for the purpose of abandoned land reclamation if the monies are deposited either into (1) a special fund under state or Indian tribal law that are expended solely for the priorities set forth in Section 403(a) after September 30, 1995, or (2) a AMD treatment and abatement fund established under state or Indian tribal law,

AMD plans provide for the comprehensive abatement of the causes and treatment of the effects of AMD within qualified hydrologic units affected by coal-mining practices. AMD plans must adhere to 30 CFR Part 876.13 and include:

- Identification of the qualified hydrological unit
- Extent of the sources of AMD within the hydrological unit
- Identification of individual projects and the measures proposed to be undertaken to abate and treat the causes or effects of AMD within the hydrological unit
- Cost of undertaking the proposed sources of funding for such measures
- Analysis of the cost-effectiveness and environmental benefits of abatement and treatment measures

In approving plans under Part 876.13, the director of the OSMRE gives priority to those plans being implemented in coordination with measures undertaken by the secretary of agriculture under the Rural Abandoned Mine Program.

National Pollutant Discharge Elimination System Permit Program

The Federal Water Pollution Control Act, commonly referred to as the Clean Water Act, enacted in 1972, established the National Pollutant Discharge Elimination System (NPDES) permit program. This program controls water pollution by regulating point sources that discharge pollutants into waters of the United States. Point sources are discrete conveyances such as pipes or human-made ditches. Although individual homes that are connected to a municipal system, use a septic system, or do not have surface discharge are not affected by this program, industrial, municipal, and other facilities are if their discharges go directly to surface waters. In most cases, the NPDES permit program is administered by authorized states. Under this program it is illegal to discharge pollutants from a point source to waters of the United States, except in compliance with an NPDES permit. The U.S. EPA and states with EPA-approved programs are authorized to issue permits.

Most states have an approved NPDES permit program, which must include technology-based effluent

limitations as well as any more stringent limitations necessary to meet water quality standards. Water quality standards, as defined in Clean Water Act Section 303(c), consist of designated uses of a water body and the water quality criteria necessary to protect those uses. The criteria can be either narrative or numeric. Under Section 303(d) of the Clean Water Act and the U.S. EPA's Water Quality Planning and Management Regulations (40 CFR Part 130), states must also submit lists of water quality–limited river segments to the U.S. EPA every two years. They must then develop total maximum daily loads (TMDLs) for those river segments that do not or are not expected to meet water quality standards. West Virginia's draft 1998 303(d) list was revised and submitted to the U.S. EPA and approved later that year. As in the case of certain river segments in West Virginia, these 303(d) lists specified that aquatic life was affected and that the primary pollution source was AMD (West Virginia Division of Environmental Protection, 1998a). Abandoned and active coal mines were the primary sources of AMD in these watersheds.

A TMDL is defined as the total amount of a pollutant that can be assimilated by a receiving water body while still achieving state water quality standards. More specifically, it is the sum of load allocations for non-point sources and waste load allocations for point sources, with a margin of safety. The final result of a TMDL analysis is a set of pollutant reduction recommendations—preferably spelled out for specific sources—that is predicted to be sufficient to bring impaired water bodies into compliance with established standards.

State-Specific Laws and Regulations: United States

California

In California, water quality standards are found in statewide and regional water quality control plans (basin plans). In addition, EPA has promulgated criteria for California in the National Toxics Rule (NTR) and the California Toxics Rule (CTR). Basin plans contain beneficial use designations, water quality objectives to protect those uses, and a program to implement the objectives. Beneficial uses and water quality objectives are the respective state equivalents of federally designated uses and criteria under Clean Water Act Section 303(c). The SIP establishes implementation provisions for NTR and CTR priority pollutant criteria and for priority pollutant objectives established in basin plans. With respect to the pollutants at issue in the permit, arsenic, cadmium, copper, lead, nickel, and zinc are priority pollutants, whereas cobalt, iron, and manganese are not. Thus, the SIP applies to the former group of pollutants but not the latter.

California addresses abandoned and inactive mine sites through the Surface Mining and Reclamation Act of 1975 (SMARA), which is overseen by the California State Mining and Geology Board (SMGB). The purpose of SMARA is to provide the lead agencies with the tools to compel reclamation activities and provide guidance for environmental restoration of former mine sites. The issues faced by the SMGB to enforce mine reclamation laws are typical of the challenges that many states and countries have. A thorough study was performed by the SMGB to evaluate the reasons for compliance issues with mining reclamation laws in California, which are described by Testa (2011).

Although SMARA defines reclamation and site restoration activities, some operators without production for 10 years still claim to be “active,” thereby avoiding costly reclamation tasks. Other mines have reported as “closed—no intent to resume,” yet the sites have not started reclamation activities. The current definition of “idle” relies solely on mineral production. The intent of SMARA and other similar legislation in other states is to have mine owners reclaim mine lands. Mineral production words such as *active*, *inactive*, *idle*, *closed*, *abandoned*, and other terms need more clarification, possibly through

legislative action. An overhaul of the federal and state mining laws is clearly needed to provide better language and financial assurances in place so that mine reclamation occurs when production ceases and mines are closed. A major impediment facing local and state regulatory agencies in implementing site restoration for idle or abandoned mine sites is that of inadequate reclamation plans. Even more important, many mines have inadequate financial assurances and a lack of available cleanup funding (Testa, 2011).

Pennsylvania

In Pennsylvania, environmental impacts from coal mining resulted in the passage in 1913 of Act 375, which prohibited the discharge of anthracite coal, culm, or refuse into streams. In 1937 the Clean Stream Law was passed, largely to protect streams from general pollution, but in 1945, included AMD.

The Explosive Safety Acts were enacted in 1937 and 1957 to regulate the use, storage, and handling of explosives, primarily to prevent drainage from mining operations. With the passing of SMCRA in 1945 and the amended Clean Stream Law of 1945, the basis for environmental regulations covering coal-mining operations throughout the state was in place. SMCRA presented the first comprehensive attempt to regulate surface coal mining. SMCRA requires coal operators and regulators to predict whether AMD may occur on a potential mine site before disturbance has begun. This requires a thorough understanding of the various components of a mine site, including overburden geochemistry, overburden handling and placement as backfill during reclamation, including method and precision, and postmining hydrology of the site.

The Anthracite Coal Mine Act was passed in 1965 to establish a program to prevent pollution from anthracite mining. By 1968, a $500 million bond was passed, in part, to finance reclamation of abandoned mine lands, and it allowed the state to purchase land for conservation and recreation purposes. Control of pollution from coal refuse piles was addressed by the Coal Refuse Disposal Control Act. In 1985, the law was amended to include a definition of AMD as an industrial waste and requiring all mines to treat their drainage to specified standards.

In 1965, Pennsylvania's Clean Streams Law was also modified to regulate discharges from coal-mining operations, while nationally, the Surface Mining Control and Reclamation Act of 1977 and the Clean Water Act of 1972 required mining operations to obtain a permit to treat water for AMD before it is discharged into natural aquatic ecosystems. SMCRA was amended in 1992 to better protect water supplies and provide incentives for re-mining of abandoned areas. SMCRA was amended again in 1996 to encourage private reclamation of abandoned mine lands through re-mining.

International Laws and Regulations

Australia

In 1995, the Australian and New Zealand Mineral and Energy Council (ANZMEC) published a baseline environmental guideline for operating mines in Australia, which required the need for acid generation to be predicted and incorporated in the mine closure plan (ANZMEC, 1995, 2000). To better understand the impact of AMD in Australia and to provide the basis for assessing long-term management options, the Office of the Supervising Scientist and the Australian Centre for Minesite Rehabilitation Research initiated the preparation of a status report on AMD. Results from the survey (Harries, 1997) suggest that about 54 sites in Australia were managing significant amounts of potentially acid-generating wastes, where “significant amounts” means that more than 10% of the waste is potentially acid generating or there is more than 10 million metric ton (mt) of potentially acid-generating wastes. About 62 additional sites

were managing some potentially acid-generating wastes but less than 10% of the total wastes and less than 10 mt.

Canada

In Canada, a survey of metal-mine and industrial-mineral tailings in 1994 showed that of the 7 billion tons of tailings and 6 billion tons of waste rock, 1.9 billion tons of tailings and 750 million tons of waste rock were potentially acid generating (MEND, 1995). An estimated 351 million mt of waste rock, 510 million mt of sulfide tailings, and more than 55 million mt of other mining sources have the potential to cause AMD (Speart, 1995). Cleanup at existing acid-generating mine sites in Canada will cost an estimated $2 to $5 billion (Government of Canada, 1991, pp. 10–11). The British Columbia 1993 State of the Environment Report estimated 240 million mt of acid-generating waste rock and 72 million mt of acid-generating mine tailings in the province. In addition, each year the stockpile of acidic and heavy metal-generating tailings and waste rock from mining in the province increases by 25 million mt (Price and Errington, 1997).

The Canadian Mine Environment Neutral Drainage (MEND) program was established by mines and provincial, territorial, and federal government agencies in 1989 in response to the recognition that AMD was the main environmental problem facing the Canadian mining industry. Mine operators were required to establish trust funds to cover the cost of the effect of AMD from mine wastes.

In British Columbia, regulations for preventing and managing impacts from mine wastes are dispersed among a number of acts, including the federal Fisheries Act, British Columbia Waste Management Act, British Columbia Mines Act, and both the British Columbia and Canadian Environmental Assessment acts. Federal and provincial budget reductions, however, have had an impact on the ability to administer, monitor, and enforce existing laws and policies, resulting in ongoing water quality and waste management problems.

In 1993, the British Columbia State of the Environment Report noted mine drainage as “one of the main sources of chemical threats to groundwater quality” in the province. Groundwater supplies drinking water for more than half the people living outside Greater Victoria and Greater Vancouver. As of 1991, the Canadian mining industry generated 1 million mt of waste rock and 050,000 mt of tailings per day, totaling 650 million mt of waste per year (Government of Canada, 1991, pp. 11–19).

Germany

Historic mining for uranium occurred in the former East German states of Saxony and Thuringia. The legacy of uranium mining in Germany includes 1400 km of open mine workings, 311 million m^3 of waste rock, and 160 million m^3 of radioactive sludges (tailings) which are located in densely populated areas. Following the reunification of Germany in 1990, a federally owned company, Wismut Gmbh, was formed, and a fund of €6.6 billion (later revised to €6.2 billion) was established under the ‘Wismut Act,” passed by the federal parliament in 1991 (Hagen and Jakubick, 2005, 2006). Although extremely costly, the Wismut rehabilitation exercise has stimulated the economy in a relatively economically depressed area of Germany. Other spin-offs have included the development of expertise and technologies in local research institutions and consulting groups, which are transferrable to other areas and have been applied successfully in Central and Eastern Europe, Russia, and Central Asia (Hagen and Jakubick, 2006). An important focus of the program has been the productive utilization of reclaimed areas, and while some land-use restrictions exist, a number of successful projects have been undertaken.

South Africa

A number of areas within South Africa are faced with AMD issues, including the Witwatersrand gold fields, the Mpumalanga and KwaZulu–Natal coal fields, and the O'Kiep copper district. The western, central, and eastern basins are identified as priority areas requiring immediate action because of the lack of adequate measures to manage and control the problems related to AMD, the urgency of implementing intervention measures before problems become more critical, and their proximity to densely populated areas. The situation in other mining regions of the country requires additional information, monitoring, and assessments of risk, particularly in vulnerable areas such as the Mpumalanga coal fields, where the impact of mining on the freshwater sources in the upper reaches of the Vaal and Olifants river systems is of serious concern.

The key factors that differentiate the developing problem in South Africa from the international examples cited and identified are the degree of interconnection of large voids, the sheer scale of the Witwatersrand operations, and the fact that many of the problem areas are located in or close to major urban centers. This necessitates large-scale programs to address the environmental problems associated with acid mine drainage.

References and Suggested Reading

ANZMEC, 1995. Baseline Environmental Guidelines for New and Existing Mines. (Report 95-02.) Australian and New Zealand Mineral and Energy Council, Canberra, Australia, 11 pp.

ANZMEC, 2000. Strategic Framework for Mine Closure. Australian and New Zealand Mineral and Energy Council, Canberra, Australia, 32 pp. Retrieved September 17, 2013: http://www.dmp.wa.gov.au/documents/Shed_env_guide_closure.pdf.

Government of Canada, 1991. The State of Canada's Environment. Ministry of Supply and Services, Ottawa, ON, Canada.

Hagen, M., and Jakubick, A.T., 2005. Returning the WISMUT legacy to productive use. In: Proceedings of Uranium in the Aquatic Environment: Uranium Mining and Hydrogeology IV (UMH-4), 4th International Conference, B.J. Merkel and A. Hasche-Berger, eds., Freiberg, Germany, September 11–16, pp. 11–26.

Hagen, M., and Jakubick, A.T., 2006. Returning the WISMUT Legacy to Productive Use: Uranium in the Environment, B.J. Merkel and A. Hasche-Berger, eds., Springer-Verlag, Berlin, pp. 11–26.

Harries, J., 1997. Acid Mine Drainage in Australia: Its Extent and Potential Future Liability. Supervising Scientist Report 125. Australian Centre for Minesite Rehabilitation Research, Kenmore, Australia.

MEND, 1995. Economic Evaluation of Acid Mine Drainage Technologies. MEND Report 5.8.1. Energy Mines and Resources Canada, Ottawa, ON, Canada.

Price, B., and Errington, J., 1997. Draft Guidelines for Metal Leaching and Acid Rock Drainage at Mine Sites in BC., British Columbia Ministry of Employment and Investment, Victoria, BC, Canada.

Speart, J., 1995. A lust for gold. Mother Jones, January–February, p. 60.

Testa, S.M., 2011. A Review of Issues Pertaining to Idle Mines Under the Surface Mining and Reclamation Act. Information Report 2010-07. State Mining and Geology Board, Natural Resources Agency, Department of Conservation, Sacramento, 25 pp.

Testa, S.M., and Pompy, J.S., 2007. Report on Backfilling of Open-Pit Metallic Mines in California. Information Report 2007-02. State Mining and Geology Board, Natural Resources Agency, Department of Conservation, Sacramento, CA.

U.S. Bureau of Land Management, 2008. Abandoned Mine and Site Cleanup Module Database, letter, September 3, 2008. http://www.blm.gov/wo/st/en/info/regulations/Instruction_Memos_and_Bulletins/national_instruction/200189.html. Retrieved September 17, 2013.

U.S. Geological Survey, 2007. Integrated Investigations of Environmental Effects of Historical Mining in the Animas River Watershed, San Juan County, Colorado, S.E. Church, P. von Guerard, and S.E. Finger, eds. U.S. Geological Survey Professional Paper 1651, 1096 pp., 6 plates, 1 DVD. http://pubs.usgs.gov/pp/1651/. Retrieved September 17, 2013.

West Virginia Division of Environmental Protection, 1998a. West Virginia 1998 303(d) List Draft. News release dated June 17.

PART IV
REMEDIATION OF ACID MINE DRAINAGE, ROCK DRAINAGE, AND SULFATE SOILS

29
Overview Of Acid Mine Drainage Treatment With Chemicals

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Acid Mine Drainage Formation

Acid mine drainage (AMD) forms when sulfide minerals in rocks are exposed to oxidizing conditions in coal and metal mining, highway construction, and other large-scale excavations. There are many types of sulfide minerals, but iron sulfides, pyrite and marcasite (FeS_2), are the predominant AMD producers (Evangelou, 1995; Skousen et al., 1999). Upon exposure to water and oxygen, sulfide minerals oxidize to form acidic and iron- and sulfate-rich drainage. The drainage quality emanating from underground mines or backfills of surface mines is dependent on the acid-producing (sulfide) and alkaline (carbonate) minerals contained in the disturbed rock. In general, sulfide-rich and carbonate-poor materials are expected to produce acidic drainage. In contrast, alkaline-rich materials, even with significant sulfide concentrations, often produce alkaline conditions in water (Skousen et al., 2002).

Acidity in AMD is comprised of both mineral acidity (iron, aluminum, manganese, and other metals, depending on the specific geological setting and metal sulfide) and hydrogen ion acidity. Approximately 20,000 km of streams and rivers in the United States are degraded by AMD. About 90% of the AMD reaching streams originates in abandoned surface and deep mines. Since no company or individual claims responsibility for reclaiming abandoned mine lands (AMLs), no treatment of the AMD occurs and continual contamination of surface water and groundwater resources results. Research shows that acid concentrations decline over time due to natural amelioration and weathering, and that the acidity decline can be predicted (Mack et al., 2010). The decline over time is important in determining the right treatment techniques (active or passive) and the length of time for treatment.

Chemical Treatment Of Acid Mine Drainage

Since the passage of the Surface Mining Control and Reclamation Act (SMCRA) in 1977, in the U.S., coal mine operators have been required to meet environmental land reclamation performance standards established by federal and state regulatory programs. Operators must also meet water quality standards established in the Clean Water Act of 1972 (CWA), which regulates discharges into waters of the United States Control of AMD is a requirement imposed on operators by both SMCRA and CWA. In addition to the surface mining permit, each mining operation in the U.S. must be issued a National Pollutant Discharge Elimination System (NPDES) permit under CWA. Allowable pollutant discharge levels are usually determined by the U.S. Environmental Protection Agency's (EPAs) technology-based standards, or the discharge levels may be based on the more stringent water quality–based standards for discharges released into streams with designated uses. If a total maximum daily load (TMDL) has been developed for a stream, load allocations from a specific point discharge may be assigned. If AMD problems develop during mining or after reclamation and if discharge limits are exceeded, a plan to treat the discharge must be developed. Treatment of AMD includes neutralization of acidity and precipitation of metal ions to meet the relevant effluent limits. In most cases, a variety of alternative treatment methods can be employed to meet the limits specified.

NPDES permits on surface mines usually require monitoring of pH, total suspended solids, and iron and manganese concentrations. Other parameters may be requested by the regulatory authority in a particular mining situation. However, in order for an operator to make a selection of an AMD treatment system, one must determine (in addition to the noted parameters above) the flow rate, the receiving stream's flow and quality, the availability of electrical power, the distance from chemical addition to where the water enters a settling pond, and the settling pond's volume for water retention time. After evaluating these variables over a period of time, the operator can consider the economics of different chemicals and alternative AMD treatment systems. Special circumstances such as the treatment of trace elements (e.g., selenium, arsenic) in the water may require a specialized treatment system that includes filtration techniques or reverse osmosis (Sandy, 2010), which are generally much more expensive to install and operate than are traditional alkaline addition and precipitation.

Typical AMD chemical treatment systems consist of an inflow pipe or ditch, a storage tank or bin holding the treatment chemical, a means of controlling its application rate, a settling pond to capture precipitated metal oxyhydroxides, and a discharge point. The latter is the point at which NPDES compliance is monitored. The amount of chemical needed for neutralization can be calculated by multiplying the flow (gal/min), the AMD's acidity (mg/L), and a factor of 0.0022. The product is the tons of acid that require neutralization per year (calcium carbonate equivalent). This value (tons of acid/yr) can then be multiplied by a conversion factor for each chemical to determine the amount of the chemical needed.

Chemicals Available to Treat AMD

Six primary chemicals have been used to treat AMD (Table 29.1). Each chemical has characteristics that make it more or less appropriate for a specific condition. The best choice among alternatives depends on both technical and economic factors. The technical factors include acidity levels, flow, the types and concentrations of metals in the water, the rate and degree of chemical treatment needed, and the final water quality desired. The economic factors include the price of reagents, labor, machinery, and equipment, the number of years that treatment will be needed, the interest rate, and risk factors.

Table 29.1 Chemical Compounds Used In AMD Treatment

			Conversion	Neutralization	2010 Cost[c]
Common Name	**Chemical Name**	**Formula**	**Factor[a]**	**Efficiency[b] (%)**	**($/ton or gal)**
Limestone	Calcium carbonate	$CaCO_3$	1.00	30	60/ton
Hydrated lime	Calcium hydroxide	$Ca(OH)_2$	0.74	90	275/ton
Pebble quicklime	Calcium oxide	CaO	0.56	90	355/ton
Soda ash	Sodium carbonate	Na_2CO_3	1.06	60	840/ton
Caustic soda (solid)	Sodium hydroxide	NaOH	0.80	100	1240/ton
Liquid caustic 20%	Sodium hydroxide	NaOH	784	100	0.95/gal
Liquid caustic 50%	Sodium hydroxide	NaOH	256	100	2.35/gal
Ammonia	Anhydrous ammonia	NH_3	0.34	100	1000/ton

[a]The conversion factor may be multiplied by the estimated tons acid/yr to get tons of chemical needed for neutralization per year. For liquid caustic, the conversion factor gives gallons needed for neutralization.

[b]The neutralization efficiency estimates the relative effectiveness of the chemical in neutralizing AMD acidity. For example, if 100 tons of acid/yr was the amount of acid to be neutralized, it can be estimated that 82 tons of hydrated lime would be needed to neutralize the acidity in the water [100(0.74)/0.90].

[c]The chemical price depends on the quantity being delivered. Caustic prices are for gallons; others are in tons.

Metal Precipitation and pH

Enough alkalinity must be added to raise water pH and supply hydroxides (OH^-) so that dissolved metals in the water will form insoluble metal hydroxides and settle out of the water. The pH required to precipitate most metals from water ranges from pH 6 to 9 (except ferric iron, which precipitates at about pH 3.5). The types and amounts of metals in the water therefore heavily influence the selection of an AMD treatment system. Ferrous iron converts to a solid bluish-green ferrous hydroxide at pH ≥ 8.5. In the presence of oxygen, ferrous iron oxidizes to ferric iron, and ferric hydroxide forms a yellowish-orange solid (commonly called “yellow boy”), which precipitates at pH > 3.5. In oxygen-poor AMD, where iron is primarily in the ferrous form, enough alkalinity must be added to raise the solution pH to 8.5 before ferrous hydroxide precipitates.

A more efficient way of treating high ferrous AMD is first to aerate the water (also outgasing CO_2), causing the iron to convert from ferrous to ferric iron, and then adding a neutralizing chemical to raise the pH above 3.5 (preferably to pH 6.0) to form ferric hydroxide. Aeration after chemical addition is also beneficial. Aeration before and after treatment usually reduces the amount of neutralizing reagent necessary to precipitate iron from AMD. Aluminum generally forms aluminum hydroxide, which precipitates at pH ≥ 5.0, but the aluminum can reenter solution again at pH 9.0. Manganese precipitation is variable due to its many oxidation states, but will generally precipitate at a pH of 9.0 to 9.5. Sometimes, however, a pH of 10.5 is necessary for complete removal of manganese. As this discussion demonstrates, the appropriate treatment chemical can depend on both the oxidation state and concentrations of metals in the AMD (U.S. Environmental Protection Agency, 1983).

Interactions among metals also influence the rate and degree to which metals precipitate. For example, iron precipitation will largely remove manganese (and many other dissolved elements) from the water at pH values below 8, due to coprecipitation, but only if the iron concentration in the water is much greater

than the manganese content (about four times more or greater). If the iron concentration in the AMD is less than four times the manganese content, manganese may not be removed by coprecipitation and a solution pH of ≥ 9 is necessary to remove the manganese to compliance levels. Because AMD contains multiple combinations of acidity and metals, each AMD is unique and its treatment by these chemicals varies widely from site to site. For example, the AMD from one site may be completely neutralized and contain no dissolved metals at a pH of 8.0, whereas another site may still have metal concentrations that do not meet effluent limits even after the pH has been raised to 10.

Limestone

Limestone has been used for decades to raise pH and precipitate metals in AMD. It has the lowest material cost and is the safest and easiest of the AMD chemicals to handle. Unfortunately, its successful application has been limited due to its low solubility and tendency to develop an external coating, or armor, of ferric hydroxide when added to AMD. In cases where pH is low and mineral acidity is also relatively low (low metal concentrations), finely ground limestone may be dumped in streams directly, or the limestone may be ground by water-powered rotating drums and metered into the stream (Zurbuch, 1996). These applications have been tried recently in West Virginia and in AMD-affected streams with great success (Brown, 2005). Limestone has also been used to treat AMD in anaerobic (anoxic limestone drains) and aerobic environments (open limestone channels) (Skousen et al., 2000). The latter two techniques are especially useful in situations where specific discharge limits do not have to be met. They are both being installed on abandoned mine land reclamation projects and by operators wishing to reduce chemical treatment costs and improve compliance (Skousen et al., 1999). Figure 29.1 shows a conventional acid drainage treatment system using limestone.

Figure 29.1 Limestone treatment has been used for decades in acid drainage treatment. A rotating wheel powered by water grinds the limestone gravel into powder for release into the water.

Hydrated Lime

Hydrated lime is the most commonly used chemical for treating AMD and is used to treat more than 90% of the acid mine drainage worldwide. It is sold as a powder that tends to be hydrophobic, and extensive mechanical mixing is required to disperse it in water. Hydrated lime is particularly useful and cost-effective in high-flow, high-acidity situations where a lime treatment plant with a mixer or aerator is constructed to help dispense and mix the chemical with the water (Skousen and Ziemkiewicz, 1996; Faulkner et al., 2005). However, due to the kinetics of lime dissolution and its neutralization efficiency, increasing the lime rate above that required for acid neutralization increases the volume of unreacted lime that enters the metal floc settling pond.

Hydrated lime can be purchased in 50-lb bags or in bulk. Bulk lime is preferred by mine operators due to cost and handling advantages. It can be delivered by barge, truck, or train and handled pneumatically. Proper storage of hydrated lime is important to maintain its flow characteristics and thus ensure efficient use. The appropriate silo volume depends on the daily lime requirement, but should be large enough to hold the amount of hydrate needed to last between scheduled deliveries with a safety margin to cover periodic unexpected delivery delays. The length of time that the system will be in operation is a critical factor in determining the annual cost of a lime treatment system due to the large initial capital expenditure that can be amortized over time. The topography of the site is also an important cost factor, with design and structural costs increasing as the slope of the site increases. Figures 29.2 and 29.3 show hydrated lime systems.

Figure 29.2 Hydrated lime, stored in a silo, is commonly used to treat acid mine drainage. The hydrated lime needs thorough mixing, which is accomplished using this large aerator and mixer. The solids are then settled in a large surface pond downstream of the mixer.

Figure 29.3 Hydrated lime is mixed with the acid drainage in this aeration and mixing basin, which is then drained to a large surface impoundment where suspended solids are settled.

Pebble Quicklime

Pebble quicklime, CaO, is used in conjunction with the Aquafix Water Treatment System utilizing a waterwheel concept (Jenkins and Skousen, 1993). The amount of chemical applied is dictated by the movement of the waterwheel, which causes a screw feeder to dispense the chemical. The hopper and feeder can be installed in less than an hour. This system was used initially for small and/or periodic flows of high acidity because calcium oxide is very reactive. However, waterwheels have been attached to large bins or silos for high-flow, high-acidity situations (Mills and Davis, 2000). Preliminary tests show an average of 75% cost savings over caustic systems and about 20 to 40% savings over ammonia systems. A pebble quicklime system is shown in Figure 29.4.

Figure 29.4 Pebble quicklime, CaO, is used in conjunction with the Aquafix Water Treatment System utilizing a waterwheel concept. The water turns the waterwheel, which turns an auger, releasing the chemical into the water. (From Jenkins and Skousen, 1993.)

Soda Ash

Soda ash is generally used to treat AMD in remote areas with low flow and low amounts of acidity and metals, but its use is declining. Selection of soda ash for treating AMD is usually based on convenience rather than chemical cost. Soda ash comes as solid briquettes and is gravity-fed into water by the use of hoppers mounted over a basket or barrel. The number of briquettes to be used each day is determined by the flow and quality of the water to be treated. One problem with the basket–hopper system is that the briquettes absorb moisture, causing them to expand and stick to the corners of the hopper. This hinders the briquettes from dropping into the AMD stream. For short-term treatment at isolated sites, some operators use a much simpler system employing a box or barrel with holes that allows water inflow and outflow. The operator fills the box or barrel with briquettes on a regular basis and places the box or barrel in the flowing water. This system (Figure 29.5) offers less control of the amount of chemical used.

Figure 29.5 Bags of soda ash briquettes are dumped in the hopper and water flows into the box, dissolving the solid briquettes for release. This treatment technique is particularly useful to treat acid mine drainage in remote areas where power is unavailable.

Caustic Soda

Caustic soda is often used in remote locations (e.g., where electricity is unavailable), and in low-flow, high-acidity situations. It is commonly the chemical of choice if manganese concentrations in the AMD are high. The system can be gravity fed by dripping liquid caustic directly into the AMD. Caustic is very soluble in water, disperses rapidly, and raises the pH of the water quickly. Caustic should be applied at the surface of ponded water because the chemical is more dense than water and sinks. The major drawbacks of using liquid caustic for AMD treatment are high cost and danger in handling.

Tanks housing caustic soda can range in volume from 500 to 8000 gal. Large tanks are usually placed on a cement platform to limit the tendency for the tank to slip or twist as the ground swells and contracts with temperature changes. The discharge line is fixed at the bottom of the tank and releases the caustic solution to the seep, ditch, or pond. The rate of flow is controlled by a gate valve placed at the end of the discharge line. A caustic soda treatment system is shown in Figure 29.6.

Figure 29.6 Example of a caustic soda (20% liquid) tank to treat acid mine drainage. The liquid is dispensed through the hose to poor-quality drainage for treatment.

Liquid caustic can freeze during winter months, but there are several options available to deal with the freezing problem. These include burying the caustic tank, installing a tank heater, switching from a 50% to a 20% caustic solution, using a freeze-proof solution containing some potassium hydroxide (KOH), and utilizing solid caustic. Burying a caustic tank is expensive because the operation must then comply with stringent EPA underground storage tank regulations. Heaters must be replaced often because of the corrosive effects of caustic. Of these options, the three most economical solutions are switching to a 20% caustic solution, adding some KOH, and switching to solid caustic. Switching from a 50% to a 20% caustic solution lowers the freezing point from 0°C to about −37°C. The addition of KOH (35% of the solution) also lowers the freezing point. Solid caustic, which may be delivered in 70-lb drums, beads, or flakes, is used with good success. It is possible to regulate the rate at which solid caustic dissolves by metering the flow of water into the drum. Solid caustic can be used to make liquid caustic. A 20% solution of caustic requires 1.8 lb of solid caustic to be dissolved in a gallon of water. Making a liquid solution from solid caustic is not cost-effective when liquid caustic can be purchased, but the use of solid caustic for treating AMD is cost-effective compared to soda ash briquettes.

Ammonia

Ammonia, the common term for anhydrous ammonia, is a material that must be handled carefully (Hilton, 1990). A gas at ambient temperatures, ammonia is compressed and stored as a liquid but returns to the gaseous state when released into water. In the gaseous state, ammonia is extremely soluble and reacts rapidly. It behaves as a strong base and can easily raise the pH of receiving water to 9.2. At pH 9.2, it

buffers the solution to further pH increases, and therefore very high amounts of ammonia must be added to elevate the pH beyond 9.2. Injection of ammonia into AMD is one of the quickest ways to raise water pH. It should be injected into flowing water at the entrance of the pond to ensure good mixing, because ammonia is lighter than water. The most promising aspect of using ammonia for AMD treatment is its cost, especially compared to the cost of caustic soda. A cost reduction figure of 50 to 70% can be realized when ammonia is substituted for caustic if the target pH for metal precipitation is below 9.2 (Skousen et al., 1990).

Major disadvantages of using ammonia include (1) hazards associated with handling the chemical, (2) potential biological implications, and (3) the consequences of excessive application rates (Faulkner, 1990). Specialized training and experience are important for the safe use of ammonia. Operators using ammonia are required to conduct additional analyses of discharge water where it is released into the stream and to monitor the biological conditions downstream. The extra analyses include temperature, total ammonia-N, and total acidity. An anhydrous ammonia treatment system is shown in Figure 29.7.

Figure 29.7 Anhydrous ammonia is pressurized in a tank to form a liquid. Once released, it becomes a gas and reacts quickly with acid drainage for treatment. The tank must have pressure gauges and heating elements.

Operators must be careful to inject the appropriate amount of ammonia due to the potential consequences of excessive ammonia application. Although ammonia can be effective for manganese removal in many cases, this requires careful monitoring and attention. Therefore, in situations where manganese is the element of primary concern (low iron, high manganese water), a different chemical may be more appropriate. Low flow in the receiving stream may also require the substitution of another neutralizing chemical during dry conditions due to ammonia's toxic nonionized state under these conditions (Faulkner,

1990).

Costs of Treating AMD

Costs have been developed for five AMD treatment chemicals under three sets of flow (gal/min) and acid concentration (mg/L) conditions (Table 29.2). These conditions represent a sufficiently wide range for valid comparison of the treatment systems. Calculations for treatment costs can also be run on AMDTreat, a software program available at http://amd.osmre.gov/.

Table 29.2 Costs in 2010 of Six Chemicals to Treat Acid Mine Drainage in West Virginia[a]

Conditions			
Flow (gal/min)	50	250	1,000
Acidity (mg/L)	100	500	2,500
Acid/yr (tone/yr)	11	275	5,500
Chemical			
Soda ash			
Annual reagent costs	$9,794	$244,860	$4,897,200
Repair costs	0	0	0
Annual labor	14,040	14,040	14,040
Installation costs	229	229	229
Salvage value	0	0	0
Net present value	119,401	1,294,729	24,556,429
Annualized cost	**$23,880**	**$258,946**	**$4,911,286**
Ammonia			
Reagent costs	$3,740	$93,500	$1,870,000
Repair costs	495	495	495
Tank rental	480	1,200	1,200
Annual labor	7,020	7,020	7,020
Electricity	600	600	600
Installation costs	1,936	6,357	6,357
Salvage value	0	0	0
Net present value	63,611	520,432	9,402,932
Annualized cost	**$12,722**	**$104,086**	**$1,880,586**
Caustic soda (20% liquid)			
Reagent costs	$8,193	$204,820	$4,096,400
Repair costs	0	0	0
Annual labor	7,020	7,020	7,020
Installation costs	283	5,478	5,478

Salvage value	0	0	0
Net present value	76,347	1,064,678	20,522,578
Annualized cost	**$15,269**	**$212,936**	**$4,104,516**
Pebble Quicklime			
Reagent costs	$2,187	$54,670	$1,093,400
Repair costs	500	2,500	10,000
Annual labor	6,500	11,200	11,200
Electricity	0	0	0
Installation costs	16,000	80,000	120,000
Salvage value	0	5,000	20,000
Net present value	61,934	416,850	5,673,000
Annualized cost	**$12,387**	**$83,370**	**$1,134,600**
Hydrated lime			
Reagent costs	$2,269	$55,963	$1,119,250
Repair costs	1,000	3,500	10,500
Annual labor	6,500	11,232	11,232
Electricity	3,500	11,000	11,000
Installation costs	58,400	106,000	200,000
Salvage value	5,750	7,500	25,000
Net present value	118,994	506,973	5,934,910
Annualized cost	**$23,799**	**$101,395**	**$1,186,982**

[a]The analysis is based on a five-year operation period and includes chemical reagent costs, installation and maintenance of equipment, and annual operating costs. Neutralization efficiencies were not included in the reagent cost calculation.

The costs for each technology were divided into two broad categories: installation cost and variable cost. Each of these can be broken down into several subcategories. For example, installation cost includes materials, equipment, and labor. Materials consist of piping, extra material for the system foundation, and additional site preparation. Equipment includes conventional machinery and/or actual system hardware. Labor costs are based on labor hours at a current union wage scale of $27/h. Variable cost includes reagent cost, annual labor, and maintenance. The amount of reagent was computed using acid neutralization formulas presented by Skousen and Ziemkiewicz (1996), but neutralization efficiencies were not included in the reagent calculation. Annual labor is estimated labor-hours to run the system for one year multiplied by the current union scale of $27/h. Other variable costs include repair costs and the cost of electricity (Phipps et al., 1991).

The prices for the reagents, equipment, and labor were based on actual costs to mining operators in West Virginia in October 2010. All dollar values are in 2010 U.S. dollars. The net present value (NPV) is the value of the total treatment system plus annual operating and chemical expenses over the duration of treatment specified. A rate of 6% per year was used to devalue the dollar during future years of the treatment period. The annualized cost was obtained by converting the total system cost (NPV) to an equivalent annual cost so that each system could be compared equally on an annual basis. The parameters

used in the analysis were entered in a spreadsheet and can be varied to conform to local conditions.

Use of soda ash has the highest labor requirements (10 h/ week) because the dispensers must be filled by hand and inspected frequently (Table 29.2). Caustic soda has the highest reagent cost per mole of acid-neutralizing capacity, and soda ash has the second highest. But remember, soda ash is much more inefficient than caustic in treating water. Hydrated lime treatment systems have the highest installation costs of the four technologies because of the need to construct a lime treatment plant and install a pond aerator. However, the cost of hydrated lime is low. The combination of high installation costs and low reagent cost make hydrated lime systems particularly appropriate for long-term treatment in high-flow, high-acid situations.

For a five-year treatment period, ammonia and pebble quicklime have the lowest annualized costs for a low-flow, low-acid situation (Table 29.2). Caustic was third and soda ash fourth, because of its high labor and reagent costs, and hydrated lime was last, because of its high installation costs. In the intermediate-flow, intermediate-acid case, pebble quicklime is the most cost-effective, with hydrated lime and ammonia next. Caustic soda and soda ash were double the annual cost of ammonia. In the highest-flow, highest-acidity category, pebble quicklime and hydrated lime are clearly the least costly treatment systems, with an annualized cost of $600,000 less than that for ammonia, the next best alternative. The use of soda ash and caustic is prohibitively expensive under high-flow, high-acidity conditions.

Other Aspects of AMD Treatment Technologies

Other Neutralizing Chemicals

Although the primary AMD chemicals and applications have been discussed, particular circumstances may require a different chemical, combination of chemicals, or particular management patterns to implement the most cost-effective method or to meet more stringent effluent limits. Several operators have used potassium hydroxide, magnesium hydroxide, and magna lime with good results (Table 29.3). Potassium hydroxide is used because it is safer to use than caustic and reduces the potential for overtreatment, but it is more expensive than caustic. Magnesium hydroxide and magna lime are dispensed in a manner similar to and behave like that of calcium hydroxide, but tend to be more expensive. Depending on shipping prices and location, these chemicals may be cheaper to use than other lime products.

Table 29.3 Chemicals for Acid Neutralization, Coagulation–Flocculation, and Oxidation

Name	Chemical Formula	Comments
Acid neutralization		
Limestone	$CaCO_3$	Used in anoxic limestone drains and open limestone channels.
Hydrated lime	$Ca(OH)_2$	Cost-effective reagent, but requires mixing.
Pebble quick lime	CaO	Very reactive, needs metering equipment.
Soda ash briquettes	Na_2CO_3	System for remote locations, but expensive.
Caustic soda	NaOH	Very soluble, comes as a solid in drums, beads, or flakes, or as a 20% or 50% liquid. Cheaper in the liquid form.
Ammonia	NH_3 or NH_4OH	Very reactive and soluble; also purchased as aqua ammonia.
		Similar to caustic.

Potassium hydroxide	KOH	Similar to hydrated lime.
Magnesium hydroxide	$Mg(OH)_2$	Similar to pebble quicklime.
Magna lime	MgO	Used as a neutralizer and oxidant; either powder or briquettes.
Calcium peroxide	CaO_2	Waste product of limestone industry. Active ingredient is CaO with various amounts of other constituents.
Kiln dust	CaO, $Ca(OH)_2$	Neutralization value varies with each product.
Fly ash	$CaCO_3$, $Ca(OH)_2$	
Coagulants and Flocculants		
Alum (aluminum sulfate)	$Al_2(SO_4)_3$	Acidic material, forms $Al(OH)_3$.
Copperas (ferrous sulfate)	$FeSO_4$	Acidic material, usually slower-reacting than alum.
Ferric sulfate	$Fe_2(SO_4)_3$	Ferric products react faster than ferrous products.
Sodium aluminate	$NaAlO_2$	Alkaline coagulant.
Anionic flocculants		Negatively charged surface.
Cationic flocculants		Positively charged surface.
Polyampholytes		Both positive and negative charges on surface based on pH.
Oxidants		
Calcium hypochlorite	$Ca(ClO)_2$	Strong oxidant.
Sodium hypochlorite	NaClO	Also a strong oxidant.
Calcium peroxide	CaO_2	Trapzene, an acid neutralizer.
Hydrogen peroxide	H_2O_2	Strong oxidant.
Potassium permanganate	$KMnO_4$	Very effective, commonly used.

Flocculants and Coagulants

Other chemicals used sparingly in AMD treatment include flocculants or coagulants, which increase particle settling efficiency (Table 29.3). These materials are usually limited to cases where unique metal compositions require a specialized treatment system, or where aeration and/or residence time in settling ponds are insufficient for complete metal precipitation. Coagulants reduce the net electrical repulsive forces at particle surfaces, thereby promoting consolidation of small particles into larger particles. Flocculation aggregates or combines particles by bridging the space between particles with chemicals. Bridging occurs when segments of a polymer chain absorb suspended particles, creating larger particles (U.S. Environmental Protection Agency, 1983; Skousen et al., 1993). A floc system is shown in Figure 29.8.

Figure 29.8 Flocculant being dispensed in acid mine drainage to help creat larger particles that will settle faster in a pond. Flocculants and coagulants are used where insufficient residence time is available for efficient settling.

The most common coagulants–flocculants used in water treatment are aluminum sulfate (alum) and ferric sulfate. These materials, also called *polyelectrolytes*, produce highly charged ions when dissolved in water. Anionic polymers dissolve to form negatively charged ions that are used to remove positively charged solids. The reverse occurs with cationic flocculants. Polyampholytes are neutral, but when dissolved in water they release both positively and negatively charged ions. Flocculants may be added to water as a liquid, or more commonly, placed in water as a gelatinous solid ("floc" logs).

Oxidants

Aeration is the process of introducing air into water. *Oxidation* occurs when oxygen in air combines with metals in the water. If the water is oxidized, metals generally will precipitate at lower pH values. For this reason, aeration of water can be a limiting factor in many water treatment systems. If aeration and oxidation were incorporated or improved in the treatment system, chemical treatment efficiency would increase and costs could be reduced. Oxidants (Table 29.3) are sometimes used to aid in completion of the oxidation process to enhance metal hydroxide precipitation and reduce metal floc volume. The hypochlorite products, hydrogen peroxide, and potassium permanganate are used in AMD situations and have demonstrated very effective oxidation. Calcium peroxide has been shown to oxygenate AMD as well as to neutralize acidity (Lilly and Ziemkiewicz, 1992).

Residence Time in Ponds and Floc Generation

After the addition of chemicals, treated water must flow into sedimentation ponds so that metals in the water can settle out or precipitate. Dissolved metals precipitate from AMD as a loose, open-structured mass of tiny grains called *floc*. All chemicals currently used in AMD treatment cause the formation of metal hydroxide sludge or floc. Sufficient residence time of the water, which is dictated by pond size and depth, is important for adequate metal precipitation. Hilton (1993) found pond size to be too small on most AMD treatment sites to result in complete treatment of the water and precipitation of dissolved metals. The amount of metal floc generated by AMD neutralization depends on the quality and quantity of water being treated, which in turn determines how often the ponds must be cleaned. Knowing the chemistry of the AMD being treated will help determine the general floc properties and provide an estimate of the stability of the various metal compounds in the floc.

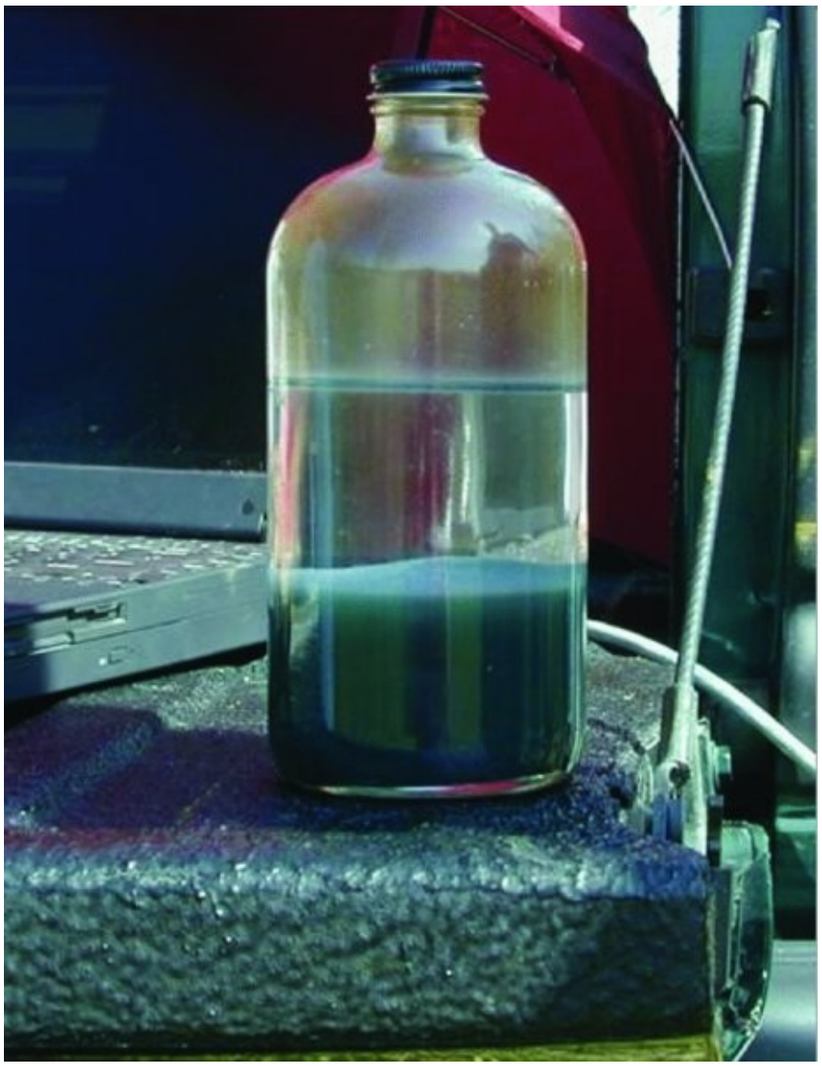

Figure 29.9 A simple jar test can be used to determine the amount of floc that will be generated after treating a certain volume of water with specific chemicals. After some time has passed to create and settle the solids, that volume of floc can be used to estimate pond sizes and floc amounts per 1000 gal of acid mine drainage.

Each floc varies chemically depending on the nature of the AMD, the neutralization chemical, and the mechanical mixing or aeration device used during chemical treatment (Ackman, 1982). The most important physical property is the floc's settleability, which includes both the settling rate and the final floc volume. The floc's settleability can be estimated by jar tests (Figure 29.9), where a specific AMD can be treated with each chemical and the floc properties can be observed and measured. Normally,

calcium hydroxide and sodium carbonate flocs are granular and dense compared to more gelatinous, loose flocs generated by sodium hydroxide and ammonia. The chemical compositions of flocs were generally composed of hydrated ferrous or ferric oxyhydroxides, gypsum, hydrated aluminum oxides, calcium carbonate, and bicarbonate, with trace amounts of silica, phosphate, manganese, copper, and zinc.

AMD neutralized by calcium hydroxide resulted in flocs containing crystalline gypsum as well as various amorphic metal hydroxides (Payette et al., 1991). AMD flocs were mostly amorphous at 1 h after formation, while crystals were observed in flocs 24 h after formation. In a series of experiments on floc generation and stability, Brown et al. (1994 a,b,c) showed that more floc was produced as the pH of the AMD solution was increased by chemical addition, and that lime flocs were more dense than sodium flocs. They also showed that volumes of floc decreased over time, due to consolidation and settling. An important finding was that aged flocs were more stable, thereby decreasing their likelihood of releasing metals (Watzlaf and Casson, 1990). The greater stability of aged flocs remained even after reintroducing the flocs into acidic solutions. Aging flocs in a dry environment resulted in greater stability than that of flocs aged under water. Figure 29.10 shows some acid mine drainage floc.

Figure 29.10 Acid mine drainage floc is composed primarily of iron hydroxides and small amounts of other metal oxyhydroxides (aluminum, manganese, and various trace elements) that were dissolved originally in the acid mine drainage. Once dewatered, they can be disposed of in surface mine backfills, underground mines, or spread on the surface for further drying.

Floc disposal options include (1) leaving the flocs submerged in a pond indefinitely, (2) pumping or

hauling flocs from ponds to abandoned deep mines or to pits dug on surface mines, and (3) dumping flocs into refuse piles. Dried flocs (pumped or dumped onto the surface of land) can be mixed with overburden during backfilling. In oxidized and dried condition, AMD flocs can become crystalline and become part of the soil. Injecting stable flocs containing excess alkalinity into acidic deep mine pools has the potential to improve the quality of the discharge from those pools. Injection into abandoned mine works is cost-effective where field conditions allow its safe disposal.

Lovett and Ziemkiewicz (1991) estimated ammonia chemical costs for a site in West Virginia at $72,000 per year and floc handling costs at $486,000 per year. Based on a flow of 100 gal/min for this site, Brown et al. (1994b) estimated that this site generated approximately 77,900 yd^3 of floc per year. Dividing $486,000 by 77,900 yd^3 of floc yields a cost of $6.25/$yd^3$ for floc handling and disposal on this site. Several mine operators observed that floc handling and disposal may cost up to $15/$yd^3$. Due to their high water content and the sheer volume of material, floc handling costs frequently exceed chemical costs severalfold.

Each AMD is unique and the chemical treatment of any particular AMD source is site specific. Each AMD source should be tested with various chemicals by titration tests or jar tests to evaluate the most effective chemical for precipitation of the metals. The costs of each AMD treatment system based on neutralization (in terms of the reagent cost and capital investment and maintenance of the dispensing system) and floc volumes and disposal should be evaluated to determine the most cost-effective system.

Summary

Acid mine drainage occurs when geological materials containing metal sulfides are exposed to oxidizing conditions. Subsequent leaching of reaction products into surface waters pollutes over 20,000 km of streams in the United States. Chemicals used to treat AMD after formation include hydrated lime, pebble quicklime, caustic soda, soda ash briquettes, and ammonia. Each chemical has advantages for certain water conditions and treatment. Under low-flow situations, pebble quicklime and ammonia are the most cost-effective. Under high-flow situations, hydrated lime and pebble quicklime are the most cost-effective, due to their low reagent cost compared to that of other chemicals. Each chemical reacts differently with a specific AMD. Therefore, it is essential that each AMD source be treated and evaluated with each chemical to determine which is most environmentally sound, efficient, and cost-effective. Coagulants and flocculants may be used in water treatment where retention time in sedimentation ponds is insufficient for metal precipitation. Oxidants can be used to meet more stringent effluent limits and to make chemical treatment more efficient. Floc, the metal hydroxides collected in ponds after chemical treatment, are disposed of in abandoned deep mines, refuse piles, or left in collection ponds. Studies show that flocs are relatively stable materials and that metals contained therein do not resolubilize after disposal, especially if aged and dried.

Acknowledgments

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References and Suggested Reading

Ackman, T., 1982. Sludge Disposal from Acid Mine Drainage Treatment. Report of Investigation 8672.

U.S. Bureau of Mines, Pittsburgh, PA.

Brown, W., 2005. In-stream limestone sand treatment of the Middle Fork Watershed. In: Proceedings of the 26th West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV. http://www.wvmdtaskforce.com/.

Brown, H., Skousen, J., and Renton, J. 1994a. Floc generation by chemical neutralization of acid mine drainage. Green Lands, vol. 24, no. 1, pp. 33–51.

Brown, H., Skousen, J., and Renton, J., 1994b. Volume and composition of flocs from chemical neutralization of acid mine drainage. Green Lands, vol. 24, no. 2, pp. 30–35.

Brown, H., Skousen, J., and Renton, J., 1994c. Stability of flocs produced by chemical neutralization of acid mine drainage. Green Lands, vol. 24, no. 3, pp. 34–39.

Evangelou, V.P., 1995. Pyrite Oxidation and Its Control. CRC Press, Boca Raton, FL.

Farley, M., 2009. Status of acid mine drainage remediation program in Ohio. In: Proceedings of the 29th West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV. http://www.wvmdtaskforce.com/.

Faulkner, B.B., 1990. Handbook for the Use of Ammonia in Treating Mine Waters. West Virginia Mining and Reclamation Association, Charleston, WV.

Faulkner, B.B., Wyatt, E.G., Chermak, J., and Miller, F., 2005. The largest acid mine drainage treatment plant in the world? In: Proceedings of the 26th West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV. http://www.wvmdtaskforce.com/.

Hilton, T., 1990. Handbook: Short Course for Taking a Responsible Environmental Approach Towards Treating Acid Mine Drainage with Anhydrous Ammonia. West Virginia Mining and Reclamation Association, Charleston, WV.

Hilton, T. 1993. Technical information for fighting acid mine drainage. In: Proceedings of the 14th West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV. http://www.wvmdtaskforce.com/.

Jenkins, M., and Skousen, J., 1993. Acid mine drainage treatment with the Aquafix system. In: Proceedings of the 14th West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV, http://www.wvmdtaskforce.com/.

Lilly, R., and Ziemkiewicz, P., 1992. Manganese removal at a lower pH with calcium peroxide: results of field trials. In: Proceedings of the 13th West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV, http://www.wvmdtaskforce.com/.

Lovett, R., and Ziemkiewicz, P., 1991. Calcium peroxide for treatment of acid mine drainage. In: Proceedings of the 2nd International Conference on the Abatement of Acidic Drainage. MEND, CANMET, Montreal, QC, Canada, pp. 35–46.

Mack, B., McDonald, L.M., and Skousen, J., 2010. Acidity decay of above-drainage underground mines in West Virginia. Journal of Environmental Quality, vol. 39, pp. 1043–1050.

Mills, J.E., and Davis, T.L., 2000. The recovery of the North Branch: 1940 to 2000 and beyond. In:

Proceedings of the 21st West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV. http://www.wvmd taskforce.com/

Payette, C., Lam, W., Angle, C., and Mikula, R., 1991. Evaluation of improved lime neutralization processes. In: Proceedings of the 2nd International Conference on the Abatement of Acidic Drainage. MEND, CANMET, Montreal, QC, Canada.

Phipps, T., Fletcher, J., and Skousen, J., 1991. A methodology for evaluating the costs of alternative AMD treatment systems. In: Proceedings of the 12th West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV. http://www.wvmdtaskforce.com/.

Sandy, T., 2010. A review of physical, chemical, and biological treatment systems for end of pipe selenium treatment. In: Proceedings of the 31st West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV. http://www.wvmdtaskforce.com/.

Skousen, J., and Ziemkiewicz, P., 1996. Acid Mine Drainage Control and Treatment. 2nd ed. National Research Center for Coal and Energy, National Mine Land Reclamation Center, West Virginia University, Morgantown, WV.

Skousen, J., Politan, K., Hilton, T., and Meek, A., 1990. Acid mine drainage treatment systems: chemicals and costs. Green Lands, vol. 20, no. 4, pp. 31–37.

Skousen, J., Lilly, R., and Hilton, T., 1993. Special chemicals for treating acid mine drainage. Green Lands, vol. 23, no. 3. pp. 34–41.

Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., and Hellier, W., 1999. Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage. Acid Drainage Technology Initiative (ADTI) of the U.S. Office of Surface Mining. Published by the National Mine Land Reclamation Center, West Virginia University, Morgantown, WV.

Skousen, J.G., Sexstone, A.J., and Ziemkiewicz, P.F., 2000. Acid mine drainage control and treatment. In: Reclamation of Drastically Disturbed Lands. Agronomy No. 41. American Society of Agronomy and American Society for Surface Mining and Reclamation, Madison, WI, Chap. 6.

Skousen, J., Simmons, J., and Ziemkiewicz, P., 2002. Acid–base accounting to predict post-mining drainage quality on surface mines. Journal of Environmental Quality, vol. 31, no. 6, pp. 2034–2044.

U.S. Environmental Protection Agency, 1983. Neutralization of Acid Mine Drainage: Design Manual. USEPA-600/2-83-001. U.S. EPA, Cincinnati, OH.

Watzlaf, G., and Casson, L., 1990. Chemical stability of manganese and iron in mine drainage treatment sludge: effects of neutralization chemical, iron concentration, and sludge age. In: Proceedings of the 1990 Mining and Reclamation Conference, West Virginia University, Morgantown, WV, pp. 3–9.

Zurbuch, P., 1996. Early results from calcium carbonate neutralization of two West Virginia rivers acidified by mine drainage. In: Proceedings of the 17th West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV. http://www.wvmdtaskforce.com/.

30
Passive Treatment of Acid Mine Drainage

Carl ZipperJeff Skousen

Acid mine drainage (AMD; also called *acid rock drainage* or *acid drainage*) is an environmental pollutant that impairs water resources in mining regions throughout the world. Where such treatment is required legally, treatment must be efficient and continuous. Treatment methods are commonly classified as either active (see Chapter 29) or passive.

Introduction

Active chemical treatment of AMD to remove metals and acidity is often an expensive, long-term liability. During the past 25 years, a variety of passive treatment systems have been developed that do not require continuous chemical inputs and that take advantage of naturally occurring chemical and biological processes to cleanse contaminated mine waters. The primary passive technologies include aerobic and anaerobic constructed wetlands, anoxic limestone drains, vertical flow wetlands (also called successive alkalinity-producing systems), limestone and slag leach beds, open limestone channels, and sulfate-reducing bioreactors. Before an appropriate system can be selected and designed, characteristics of the water to be treated must be determined. Important water characteristics are flow, acidity and alkalinity, metal concentrations, and dissolved oxygen concentration (Zipper et al., 2010).

At their present stage of development, some passive systems can be implemented as a single permanent solution for many types of AMD at much lower cost than that for active treatment. Alternatively, passive systems can furnish partial treatment that greatly improves the quality of receiving streams or greatly decreases the costs of active treatment. Relative to active chemical treatment, passive systems generally require longer retention times and greater space but markedly decrease long-term costs. Many passive systems have realized successful short-term implementation in the field and have substantially reduced or eliminated water treatment costs at many mine sites (Faulkner and Skousen, ; Skousen et al.,). Current research seeks to understand the dynamically complex chemical and biological mechanisms that occur within passive systems and that are responsible for successful AMD treatment.

Selection and design of an appropriate passive system are based on water chemistry, flow rate, and local topography and site characteristics (Hyman and Watzlaf,), and refinements in design are ongoing. Figure 30.1 summarizes current thinking as to the appropriate type of passive system for various conditions, and Table 30.1 summarizes design considerations and sizing factors. In general, aerobic wetlands can treat net alkaline water; ALDs can treat water of low Al, Fe^{3+}, and dissolved O_2 (DO); and vertical flow wetlands, anaerobic wetlands, and open limestone channels can treat net acidic water with higher Al, Fe^{3+}, and DO, as well as net alkaline water. As scientists and practitioners improve treatment predictability and longevity of passive systems, they will be better able to treat the more difficult waters of high acidity and high Al content.

Table 30.1 Design Factors for Six Passive Treatment System Types

System Type	Design Factor	References
Aerobic wetland	10 g Fe/m^2 per day	Skousen et al. (1999)
	1 g Mn/m^2 per day	Hedin et al. (2002)
Anaerobic wetland	3.5 g acidity/m^2 per day	Hedin et al. ()
Anoxic limestone drain	15 h residence time	Watzlaf (), Watzlaf et al. ()
Vertical-flow wetland	20 g acidity/m^2 per day	Kepler and McCleary (1997)
Open limestone channel	Acid load and residence time	Ziemkiewicz et al. (1997)
Limestone leach bed	2 h residence time	Skousen and Ziemkiewicz (2005)

Source: Zipper and Skousen (2010).

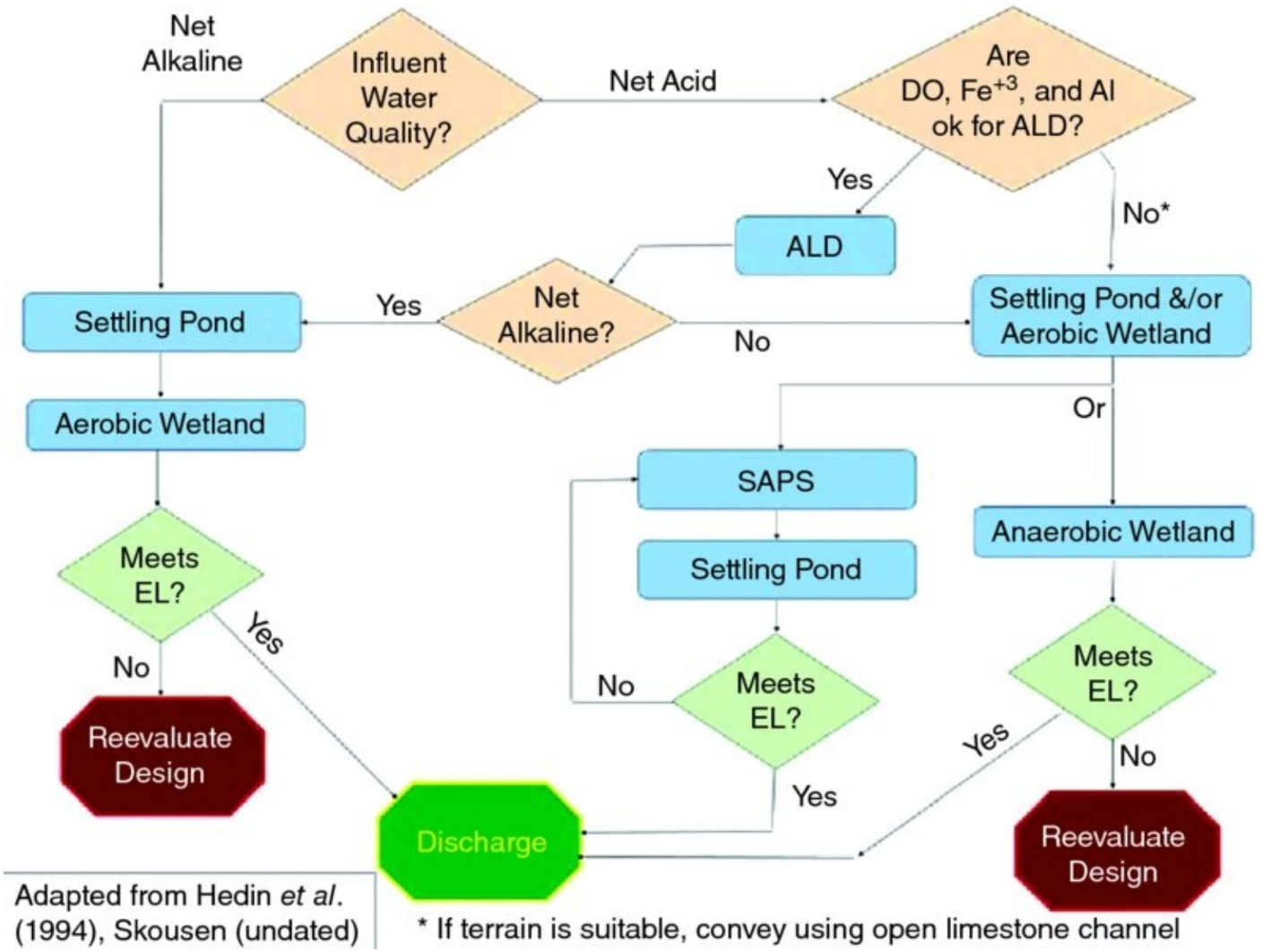

Figure 30.1 Passive system design flowchart. More detailed versions of the chart can be accessed in other sources (Hedin et al., ; Skousen and Ziemkiewicz,).

These technologies have potential application in the treatment of AMD from both coal and hardrock mining. Drainage from hardrock mining areas contains elevated concentrations of various heavy metals (copper, lead, zinc, cadmium, etc.) which contribute to overall acidity and can greatly increase the toxicity of the water, but the general nature of AMD from coal and hardrock areas is similar (e.g., acidity,

high Fe and SO_4), as are most of the problems in treatment. The processes that occur in passive systems to reduce acidity and remove metals from coal mine drainage are essentially the same as those for metal mine drainage. Discussion and case studies in this chapter focus on coal mine drainage, but many aspects can also apply to metal mine drainage.

A major problem in the treatment of AMD is removal of iron and, at many sites, manganese and aluminum. To simplify wording in the remainder of the chapter, the term *metals* will be used for these three constituents, even though the elements concerned occur as dissolved cations in the AMD and are not in the metallic state.

Passive Treatment of AMD

Huntsman et al. () and Wieder and Lang (1982) first noted the amelioration of AMD following passage through naturally occurring *Sphagnum* bogs in Ohio and West Virginia; others noted similar treatment by passage through *Typha* wetlands (Brooks et al., ; Samuel et al.,).

Aerobic Wetlands

Aerobic wetlands are the simplest type of passive treatment system but are limited in the types of waters they can treat effectively. Aerobic wetlands are used to treat mildly acidic or net alkaline waters containing elevated Fe concentrations. They have limited capacity to neutralize acidity. These systems' primary function is to allow aeration of the mine waters flowing among the vegetation so that dissolved Fe can oxidize, and to provide residence time where the water is slowed for Fe oxide products to precipitate. Because Fe precipitation generates H^+, the water leaving the aerobic wetland may be lower in pH than that entering, even if Fe concentrations are less.

Where influent waters are net alkaline and Fe is not in solution at significant concentrations, aerobic wetlands are also capable of removing manganese. However, Mn removal effectiveness is limited by several factors. Mn removal occurs via mechanisms similar to the removal of Fe, but more slowly. Dissolved Mn can oxidize to solid-phase forms, such as MnO_2 (manganese dioxide), but the process is very slow when the pH is below 8, and like Fe oxidation, it generates acidity. As with Fe, Mn oxidation occurs both chemically and microbially. However, Fe oxidation is a preferential process, so Mn oxidation does not occur as a significant process until Fe oxidation is nearly complete. Thus, for aerobic wetlands to remove Mn successfully, large areas or additional wetland cells are required.

A typical aerobic wetland system is a shallow, surface-flow wetland planted with cattails (*Typha* sp.) (Figures 30.2 and 30.3). The depression that holds the wetland may or may not be lined with a synthetic or clay barrier. Depending on landscape conditions, the lining can be intended either to keep treatment waters from draining *out* through the depression's base or to prevent environmental waters from moving *into* the system and thus diluting the waters to be treated.

Figure 30.2 Simplified cross-sectional view of an aerobic wetland.

Figure 30.3 Aerobic wetlands that are ponds with organic substrates and vegetation.

Aerobic wetland systems can treat mildly acidic, circumneutral, or alkaline waters that contain dissolved metals such as Fe, which can be transformed to the solid phase via oxidation. Aquatic plants such as cattails transport O_2 to the subsurface through their roots, which aids metal oxidation. The aquatic plants also help to prevent channelization of the waters flowing through the wetland, slowing water velocities and aiding solid-phase metal removal via sedimentation.

Substrates vary from natural soils to composted organic matter. Shallow water levels (10 to 30 cm) are generally maintained for the aerobic conditions and to enable the growth of aquatic plants, which aid wetland performance. Constructing the system with variable water depths within the range 10 to 30 cm encourages plant community diversity. Plants serve as physical obstacles which help to prevent *channelized flow*, a condition that occurs when flowing waters are concentrated within the shortest distance between the entrance and exit; thus, plants can help to disperse water flows throughout the wetland for more effective treatment. Dispersed flow causes the waters to move more slowly, allowing more time for oxidation and aiding in physical filtration and the sedimentation of small particles. In some cases, barriers or baffles are placed in a wetland to cause a tortuous water path. Species such as cattails transport O_2 from the atmosphere through their roots, which also aids oxidation. Although most aquatic plants will remove some metals from the water column, their capacity is quite limited relative to the overall metal loadings that these systems usually receive. Therefore, metal uptake by plants plays only a minor role in water treatment by these systems.

Aerobic wetlands are often designed in series with a small sedimentation basin that contains no plants. Waters to be treated may flow through the sedimentation basin prior to entering the aerobic wetland, which allows suspended sediments and easily hydrolyzable Fe^{3+} to settle out. The pretreatment basin is designed to extend the aerobic wetland's useful life by accumulating particles that would otherwise settle in the wetland system.

Commonly cited design criteria are based on the total surface area required to treat anticipated Fe and Mn loadings (Table 30.1). Because performance varies with factors such as weather and stream flow, more conservative design criteria are recommended when systems are intended to achieve regulatory compliance because the penalties for even occasional failure to perform as expected can be significant. Data from Skousen and Ziemkiewicz () demonstrate that aerobic wetland treatment systems do not always perform equivalent to the design criteria (Figure 30.4). On a total acidity basis, the design criteria for nonregulatory compliance (20 g/m^2 per day of Fe) is equivalent to about 36 g/m^2 per day of total acidity, assuming that most of the soluble iron is in Fe^{2+} form, which would be expected at pH ~ 7; while for nonregulatory compliance purposes, Fe-based design criteria would be roughly half that level (meaning that the wetland was designed to be twice as large). The aerobic wetland systems of Figure 30.4 demonstrate variable performance, with only two of the six performing within the range of design criteria for regulatory compliance and two additional systems approximating nonregulatory compliance criteria.

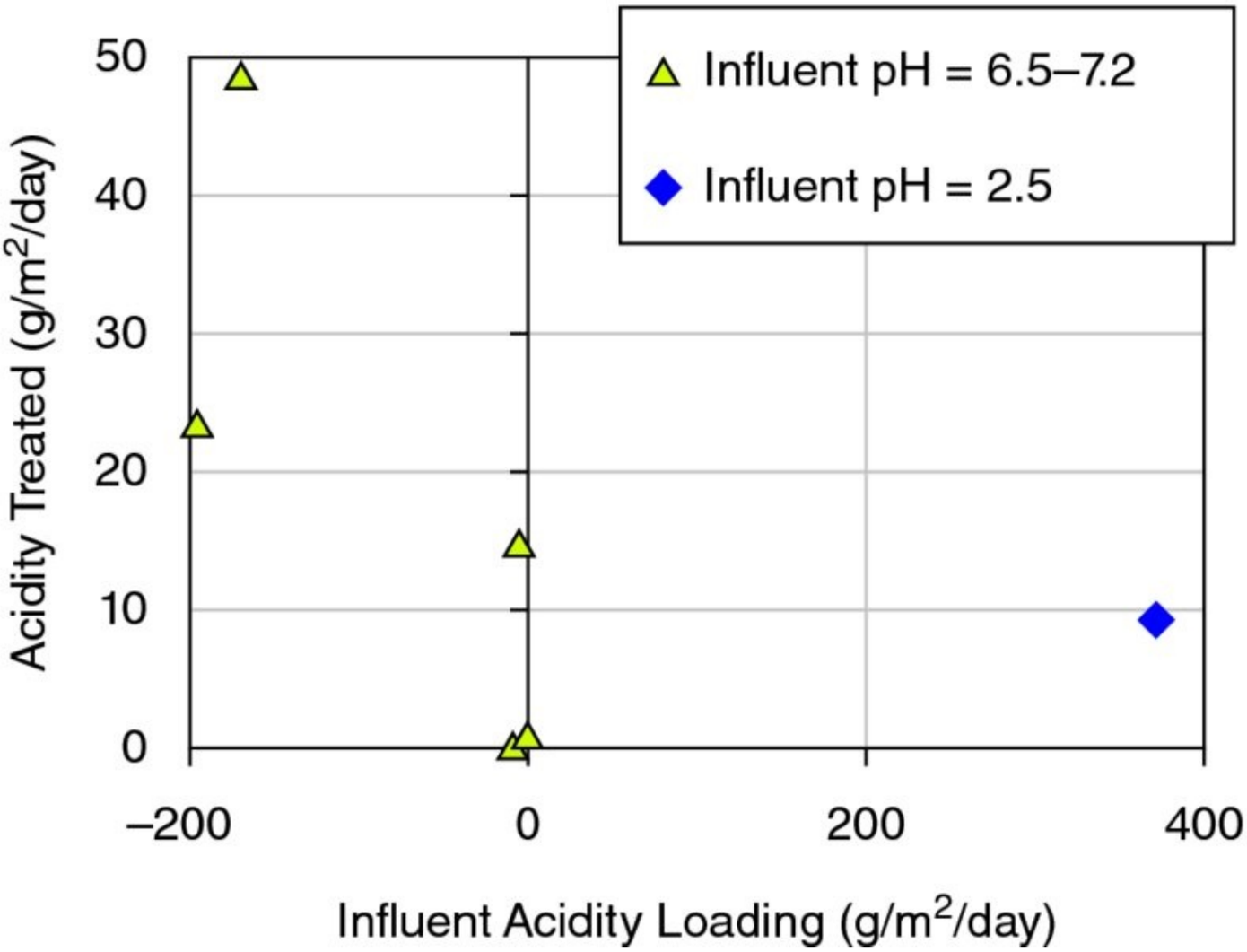

Figure 30.4 Data compiled by Skousen and Ziemkiewicz () which document the performance of six aerobic wetland systems. All values charted are averages of multiple samples collected over extended time periods.

Anaerobic Wetlands

Modifications of the aerobic wetland design enable these systems to add alkalinity so as to effectively treat net acid waters (Figure 30.5). These include the addition of a bed of limestone beneath or mixed with an organic substrate which encourages generation of alkalinity as bicarbonate (HCO_3^-). Sulfate reduction is a microbial process that occurs under anoxic (low-O_2) conditions when sulfates and biodegradable organics are present. Sulfate-reducing bacteria utilize the O_2 that enters the anoxic environment as a component of sulfate (SO_4^{2-}) for metabolic processing of biodegradable organics, transforming the associated S to either hydrogen sulfide gas (H_2S) or to a solid-phase sulfide. The most common form of sulfide reduction generates H_2S and bicarbonate alkalinity:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \quad (30.1)$$

Sulfate reduction is common in both natural and treatment wetlands, where its occurrence can often be detected as visible bubbles emerging from the substrate accompanied by the “rotten egg” odor of H_2S gas. When acid-soluble metals are in solution, sulfate reduction can form solid-phase metal sulfides as an

alternative end product, which removes metals from solution and deposits them in the substrate:

$$M + SO_4^{2-} + CH_2O \rightarrow MS + HCO_3^- \quad (30.2)$$

where M represents a sulfide-forming metal and MS represents a metal sulfide. The other alkalinity-generating process is dissolution of the limestone within or below the organic substrate:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \quad (30.3)$$

The bicarbonate ion (HCO_3^-) is a source of alkalinity and can neutralize H^+ and/or raise pH to enhance the precipitation of acid-soluble metals:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2(aq) \quad (30.4)$$

Aerobic wetland systems (Figure 30.5) are also called *composted wetlands* because the substrate layer generates alkalinity. The substrate can be comprised of biodegradable organic materials that are placed over limestone, as represented, or as an organic–limestone mixture. The circular arrows represent diffusion of treatment waters through the substrate, which generates alkalinity.

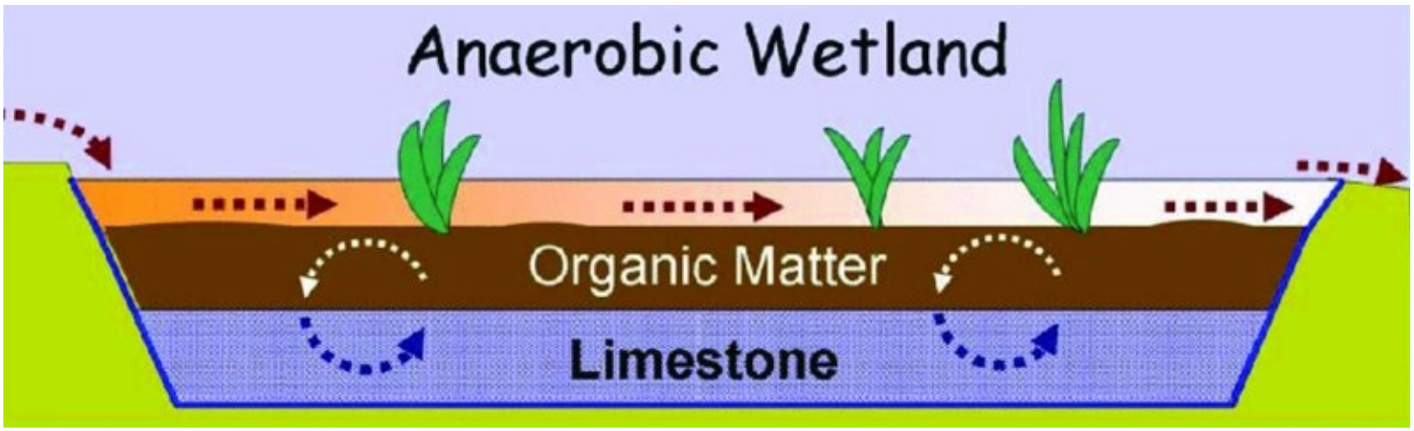

Figure 30.5 Simplified cross-sectional view of an anaerobic wetland.

High-Ca limestones, with greater than 90% $CaCO_3$, are preferred for passive treatment use because they are more soluble than impure limestones or those that contain a larger proportion of total carbonates as $MgCO_3$ (dolomitic limestones). The limestone is placed so that waters must move through organic substrate prior to contacting it, which allows bacteria in the organic material to remove O_2 from the percolating waters, which helps to prevent *armoring* of the limestone; that is, the process of coating of Fe on limestone surfaces which renders those surfaces less reactive.

Anaerobic wetlands are capable of removing acid-soluble metals, especially Fe and Al, and producing alkalinity. However, their effectiveness is limited by the slow mixing of the alkaline substrate water with acidic waters near the surface. Thus, these systems commonly require large surface areas and long retention times. Like other passive treatment systems, their effectiveness at removing Mn is limited unless very large areas are used.

Research reported by Skousen et al. () demonstrates that substrate processes—alkalinity generation to stimulate oxidation and hydrolysis, and metal sulfide formation—are the primary drivers of water quality renovation over the long term. When the systems are first constructed, mechanisms such as plant uptake and sorption by organic materials can contribute to metal removal, but the capacity of these mechanisms

to remove metals is soon exhausted as absorption sites are filled. Wetlands in a series, as shown in Figure 30.6, can remove metals sequentially.

Figure 30.6 How to place baffles in anaerobic wetlands (close-up, left) to hinder short-circuiting of water flow.

General guidelines for anaerobic wetland construction advocate use of a 30- to 60-cm layer of organic matter over a 15- to 30-cm bed of limestone, or placing a mixture of organic matter and limestone to a depth of 50 to 100 cm. The organic matter must be permeable to water and biodegradable, and materials such as spent mushroom compost have been used successfully at a number of sites in northern Appalachia. Cattails (*Typha* sp.) or other aquatic vegetation may be planted throughout the wetland to supply additional organic matter for the O_2-consuming bacteria and to promote metal oxidation with the release of oxygen from their root system. If sediments or easily hydrolyzable Fe are present in the waters to be treated, a pretreatment pond can be included in the system design.

The design depth of water over the organic–limestone mixture varies. Some anaerobic wetland designs maintain water depths of 10 to 30 cm as a means of encouraging aquatic vegetation for the purpose of preventing flow channelization and adding fresh organic material to the substrate. Other designers utilize deeper waters and do not encourage vegetation, reasoning that the translocation of oxygen to substrates through the roots of species such as cattails hinders substrate functions, which are critical to performance and require anoxic conditions. When plants are not present, physical barriers can be installed to prevent

flow channelization, and additional organic materials can be added manually (Figures 30.6 and 30.7).

Figure 30.7 Passive acid mine drainage remediation systems can be optimized by a variety of methods.

Available guidelines for system sizing recommend planning for acidity removal rates of 3.5 g/m^2 per day when the system is intended for regulatory compliance and 7 g/m^2 per day otherwise. However, performance data (Skousen and Ziemkiewicz, ; Figure 30.8) demonstrate that anaerobic wetland performance is highly variable and that these systems tend to neutralize acidity more effectively when receiving higher influent acidity concentrations and loadings. Of the 16 systems whose performance was documented, eight were removing acidity at rates of about 10 g/m^2 per day or greater.

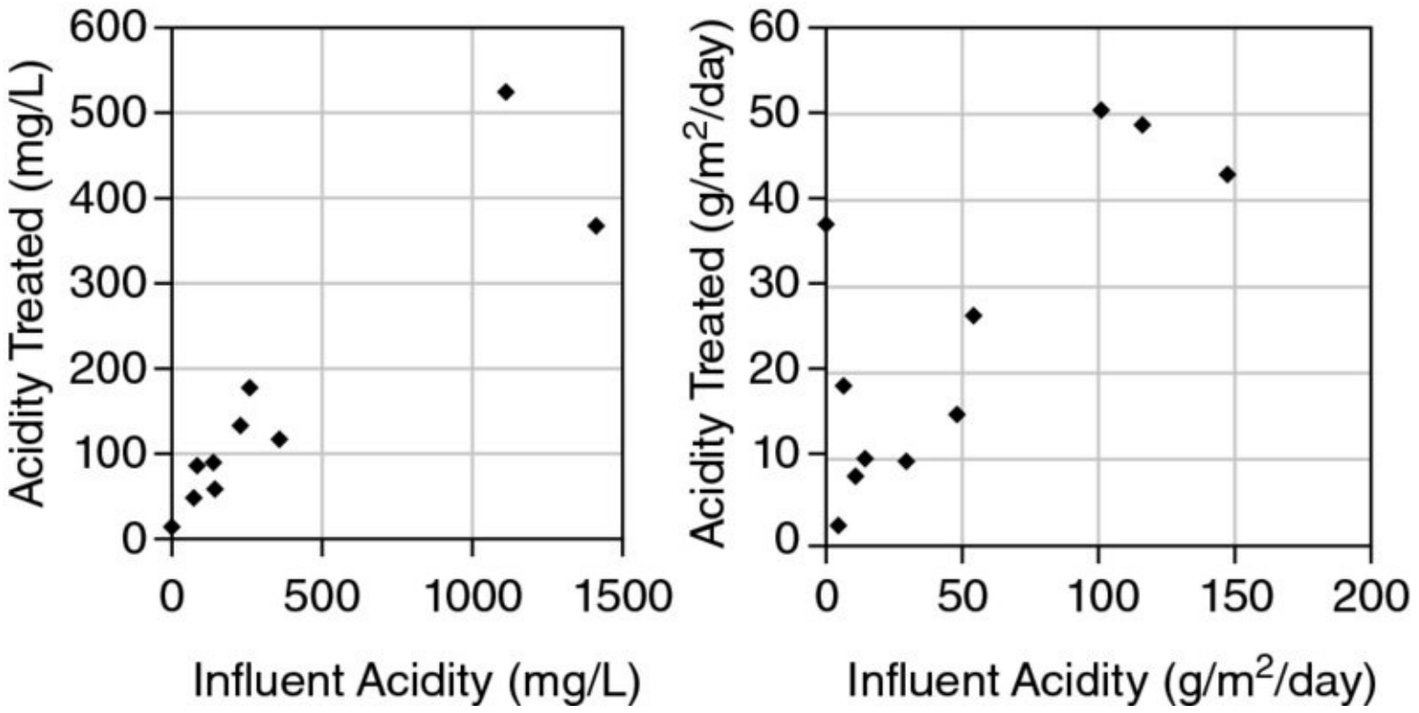

Figure 30.8 Graphs prepared from data compiled by Skousen and Ziemkiewicz () which document the performance of 11 anaerobic wetland systems.

Because poor water quality and low nutrient availability hindered plant growth in this aerobic wetland (Figure 30.7), haybales were placed to prevent flow channelization and to add biodegradable organic materials that help stimulate alkalinity generation via sulfate reduction. The inset shows iron floc accumulating on the biodegradable organic material. Water draining from an abandoned deep mine enters the system to the right of the inset and flows through the system toward an exit at the lower right.

Eleven anaerobic wetlands were evaluated by Skousen and Ziemkiewicz (). All values charted (Figure 30.8) are averages of multiple samples collected over extended time periods, and the systems represent a variety of operating conditions.

Anoxic Limestone Drains

Anoxic limestone drains (ALDs) can also be used to treat acidic waters (Figure 30.9). ALDs are limestone-filled trenches through which acidic water is directed so that the limestone can produce bicarbonate alkalinity via dissolution (Figure 30.10). ALDs are capped with clay or compacted soil to prevent AMD contact with oxygen. The effluent is held in a settling pond to allow pH adjustment and metal precipitation prior to being discharged to natural water courses. Where water quality is suitable, an ALD can be used to pretreat the AMD prior to forcing the waters through subsequent passive treatment units. Anoxic limestone drain systems (Figure 30.9) are used to add alkalinity to anoxic (low-O_2) waters that are low in constituents that can easily precipitate under low O_2 conditions (i.e., Al, Fe^{3+}). The standpipe exit is elevated, and other measures are taken to exclude O_2 from the drain so as to prevent precipitation of metals within the gravel pores.

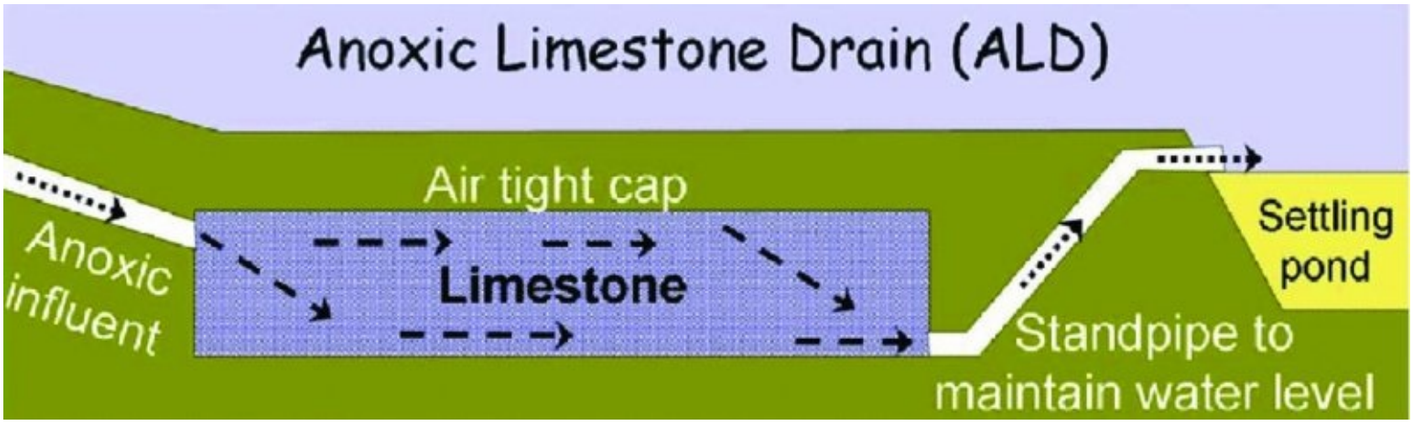

Figure 30.9 Simplified cross-sectional view of an anoxic limestone drain.

Figure 30.10 Construction of an anoxic limestone drain.

When working as intended, ALDs can renovate acidic waters more cost-effectively than can wetland-based systems. ALDs are not, however, capable of treating all AMD waters. Significant concentrations of O_2, Al, or Fe^{3+} in the water can cause an ALD to clog with metal hydroxides once a pH of 4.5 or above is reached. When excess Fe^{3+} is present in the AMD or is allowed to form from Fe^{2+} due to the presence of O_2, solid-phase Fe can precipitate within the ALD, while Al precipitation can occur as pH increases even

when O_2 is excluded.

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}H_2O \quad (30.5)$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH_{(s)} + 3H^+ \quad (30.6)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+ \quad (30.7)$$

If significant metal precipitation occurs within an ALD, the precipitant *floc* (a gel comprised of hydrolyzed solid-phase metal precipitants) will clog the ALD's pores, hindering waters from moving through the system and impairing its function (Figure 30.11). Once an ALD becomes clogged with precipitants, it becomes nonfunctional and must be replaced, repaired, or abandoned. To maximize the probability that an ALD will not clog, Fe^{3+}, Al, and dissolved O_2 concentrations of the influent waters should all be below 1 mg/L. However, Skousen et al. () suggest that ALDs can be used for AMD with dissolved O_2 concentrations of up to 2 mg/L and Al concentrations of up to 25 mg/L when less than 10% of the total Fe is in the Fe^{3+} form. Although such ALDs can be expected to clog eventually, they can still offer cost-effective water treatment compared to other passive system processes during their time of operation. ALDs are far less costly to construct than anaerobic or vertical-flow wetland treatment systems and can render less costly treatment on a life-cycle basis, even if periodic but infrequent repair and replacement are required. As shown in Figure 30.10, the plastic liner is intended to ensure that atmospheric O_2 is unable to enter the drain; it will be folded over the limestone gravel and covered with soil as the ALD construction process continues.

Figure 30.11 Anoxic limestone drains are vulnerable to plugging with metal precipitants (left), which can cause a "blowout" of water from the drain (right) if those waters are under sufficient pressure.

The term *retention time* means the amount of time the "average" quantity of water flowing through a drain spends within the drain structure, and is calculated as (total pore volume)/(average rate of flow through the drain). A common recommended design criterion is that ALDs should achieve at least 15-h retention times. This criterion is based on research conducted by Watzlaf et al. (2000), who established a series of sampling ports in several ALDs; they were able to withdraw water samples at several points so as to observe how the water quality changed as the water moved through the ALDs. They observed that alkalinity generation reached maximum levels, which was within the range of 150 to 300 mg/L (as $CaCO_3$) after 14 to 23 h of retention time. As dissolved Ca^{2+} and HCO_3 concentrations increase and approach saturation, continued limestone dissolution and alkalinity generation were hindered (Figure 30.12). As a result, standard design guidelines for ALDs generally recommend that drains be constructed to achieve 15-h retention times over their design lifetimes. Because limestone can be expected to dissolve over that lifetime, the initial construction achieves a longer retention time. An equation commonly used in ALD design is

$$M = \frac{Q\rho t}{V} + \frac{QCT}{x} \qquad (30.8)$$

In this equation, M represents the mass of limestone to be used to construct the drain. The first term on the

right represents the volume of limestone required to achieve the design retention time; the second term represents the volume of limestone expected to dissolve over the design lifetime. Adding the two quantities is intended to assure that the mass of limestone remaining in the drain throughout its design lifetime is adequate to achieve the design retention time. To calculate the first term: Q is the water flow rate, ρ the limestone density, t the design retention time, and V the bulk void volume of the limestone gravel, expressed as a percentage of total volume. To calculate the second term: Q is the influent flow rate, C the expected rate of alkalinity generation, expressed on an mg $CaCO_3$/L per unit time basis; T the design lifetime; and x the $CaCO_3$ content of the limestone, for which 90% or greater is recommended.

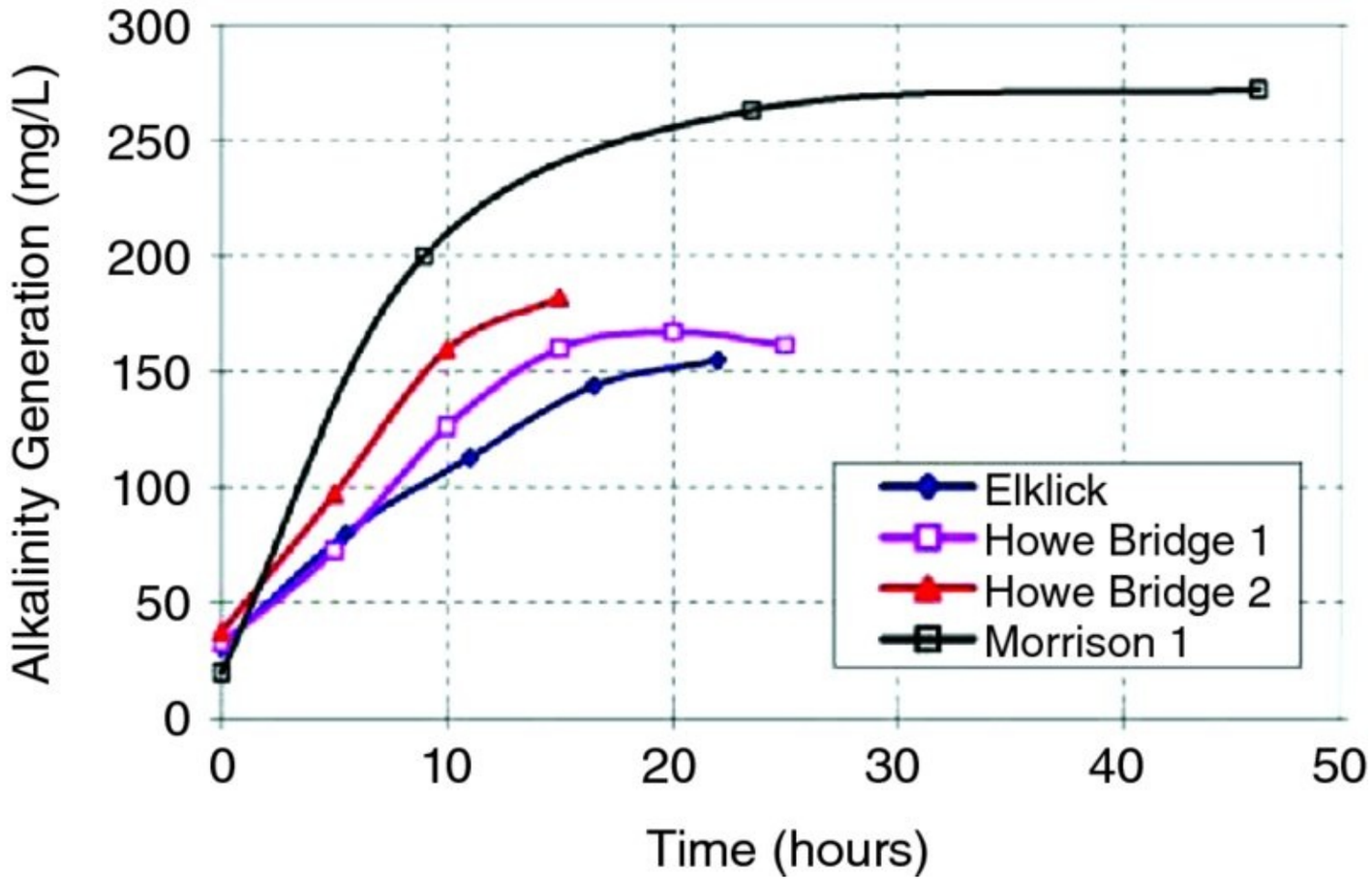

Figure 30.12 Data from Watzlaf et al. (2000) collected using water monitoring ports in four anoxic limestone drains demonstrated that alkalinity concentrations approached a maximum after 14 to 23 h in drains.

As an example calculation, consider the ALD sizing for a 120-L/min AMD flow (2 L/s) of acidic water (500 mg/L acidity, expressed as $CaCO_3$ equivalent) that meets the water quality guidelines for the use of ALDs. The amount of limestone required to provide 15 h of retention time for that flow can be calculated using the first part of equation (30.8) if we know the limestone density and porosity. A typical delivered 2- to-4 in. (5- to-10 cm) limestone product may have a density 1540 kg/m^3 (Caterpillar, Inc.,) and a porosity of 41%. Inserting these quantities into the first portion of equation (30.8) yields a calculated limestone quantity of 405 metric tons (mt). The second part of the equation can be used to calculate the quantity of limestone necessary to treat that water flow for a design lifetime. If we assume that 250 mg/L of alkalinity will be generated over a 20-year lifetime by a limestone with 90% Ca content, the equation yields a calculated quantity of 342 mt of limestone that will be dissolved over that lifetime. Therefore, the system's design size can be calculated as 747 mt. A conservative designer would add a factor of safety by

increasing the design quantity beyond that minimum. In fact, it is advisable to add an additional limestone quantity to ensure an adequate lifetime, given that the longer retention times early in the design life are likely to increase both the alkalinity generation rate and the limestone dissolution rate relative to the system's later stages. In this case, we'll assume that the designer applied his or her best professional judgment to increase the design limestone quantity to 800 mt. Recalling the limestone delivered density estimate cited above, this quantity can be translated into a covered trench volume of 519 m^3.

Critical assumptions for this calculation are the alkalinity generation rate and the design lifetime. We selected 250 mg/L as a conservative estimate for the rate of alkalinity generation considering that the influent water quality is of good quality (i.e., contains few precipitants); and it is highly acidic and therefore likely to achieve a relatively rapid rate of limestone dissolution (i.e., see Zipper and Skousen, 2010; and Figure 30.13)). The example designs for a 20-year lifetime assuming that the site manager desires a long-term treatment solution but also considering that the influent water quality is well suited to ALD requirements. If the water were not as well suited, designing for a shorter life would be logical given the additional costs of excavating to procure the larger limestone volume necessary for a longer design life and the additional costs that would be required to excavate, dispose of, and replace that larger volume when the precipitants do eventually clog the drain.

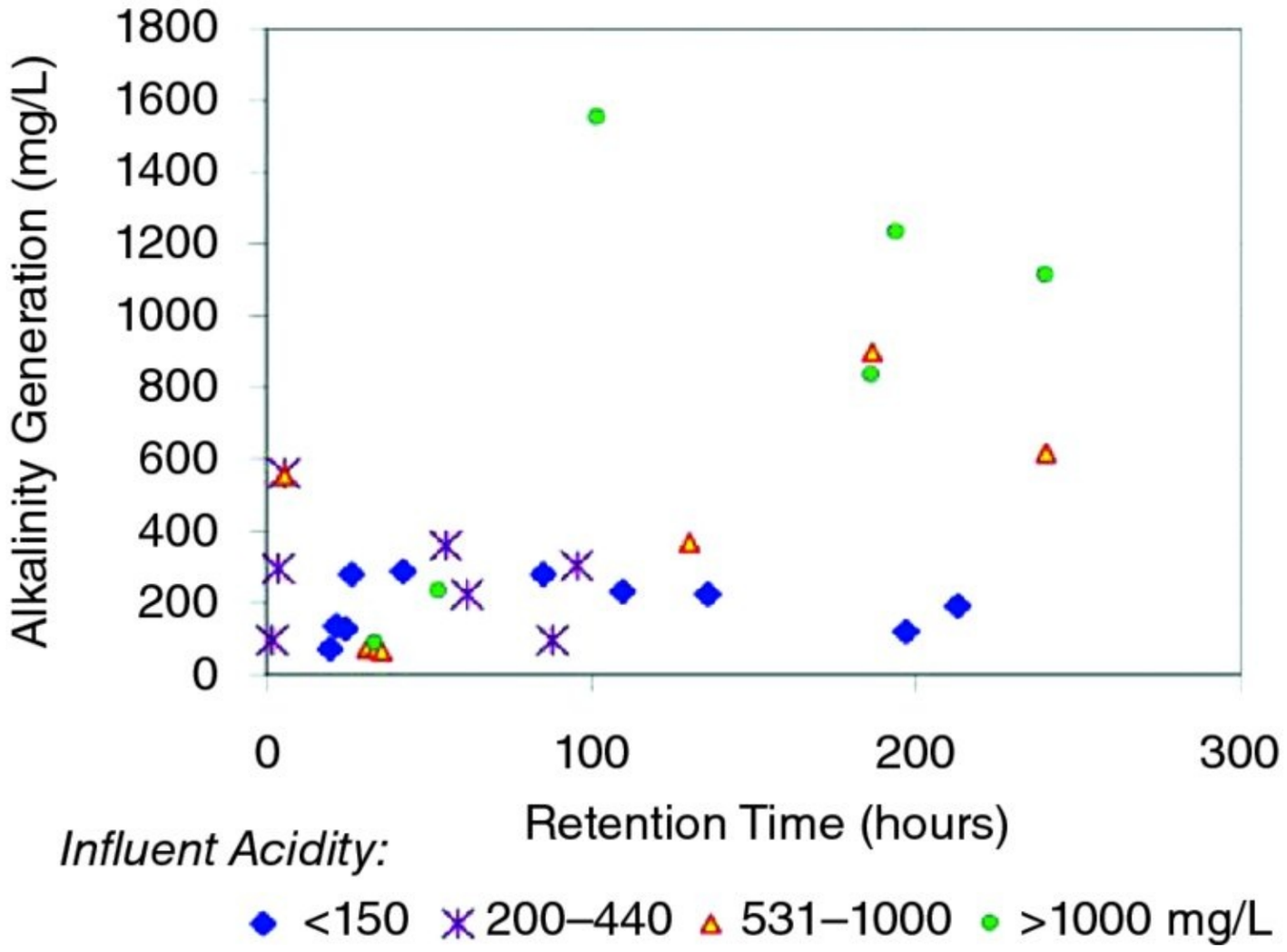

Figure 30.13 Data compiled by Skousen and Ziemkiewicz () document the performance of 36 anoxic limestone drains.

As a result of a study by Watzlaf et al. (2000), design guidelines for ALDs generally recommend that

drains be constructed to achieve 15-h retention times over their design lifetimes. Average influent acidities (mg/L as $CaCO_3$) were 52 at Elklick, 382 at Morrison, and 472 and 411 at Howe Bridge 1 and 2, respectively. Passive and semipassive coal mine drainage systems have been discussed by Watzlaf et al., (2004a,b).

ALD performance data compiled by Skousen and Ziemkiewicz () demonstrate that like other passive treatment systems, ALD performance is highly variable (Figure 30.13). Twenty of the 36 ALDs had estimated average influent acidities of 440 mg/L or less, close to the range of systems used to generate the 15-h retention time design guideline. All generated alkalinities of 400 mg/L or less, and most were close to or within the 150 to 300 mg/L alkalinity target range. However, 14 of the ALDs documented were treating waters with influent acidities of 591 mg/L or greater, and most of these systems were generating alkalinities considerably above the commonly cited 150 to 300 mg/L target range; among this group, those with longer retention times tended to generate the most alkalinity.

All values charted in Figure 30.13 are averages of multiple samples collected over extended time periods. All but one of the systems with influent acidities of 440 mg/L or less generated less than 400 mg/L alkalinity, regardless of retention time. Six of the systems with higher influent acidities, primarily those with longer retention times, demonstrated greater alkalinity generation performance. Three of the systems documented failed to generate alkalinity and are not represented.

Open Limestone Channels

An open-air analog to the ALD is the open limestone channel (OLC). These systems are employed where AMD must be conveyed over some distance prior to or during treatment. OLCs are simple to construct and operate if the terrain is favorable. OLCs require an open channel lined with high-Ca limestone to convey AMD to an outlet. Even though the limestone typically becomes armored with Fe, the armored limestone retains some treatment effectiveness. OLCs are most effective when placed on slopes of greater than 15% or when they receive periodic high flows, as the abrasive action of fast-moving water and suspended particles tends to dislodge the Fe armoring, refreshing the surface for treatment effectiveness (Figure 30.14). OLCs can be effective as one element of a passive treatment system (Figure 30.15), but typically are not relied upon for stand-alone AMD treatment (Ziemkiewicz et al., 1997; Skousen et al.,). All values charted in Figure 30.15 are averages of multiple samples collected over an extended period.

Figure 30.14 Open limestone channels are more effective on slopes of greater than 15%.

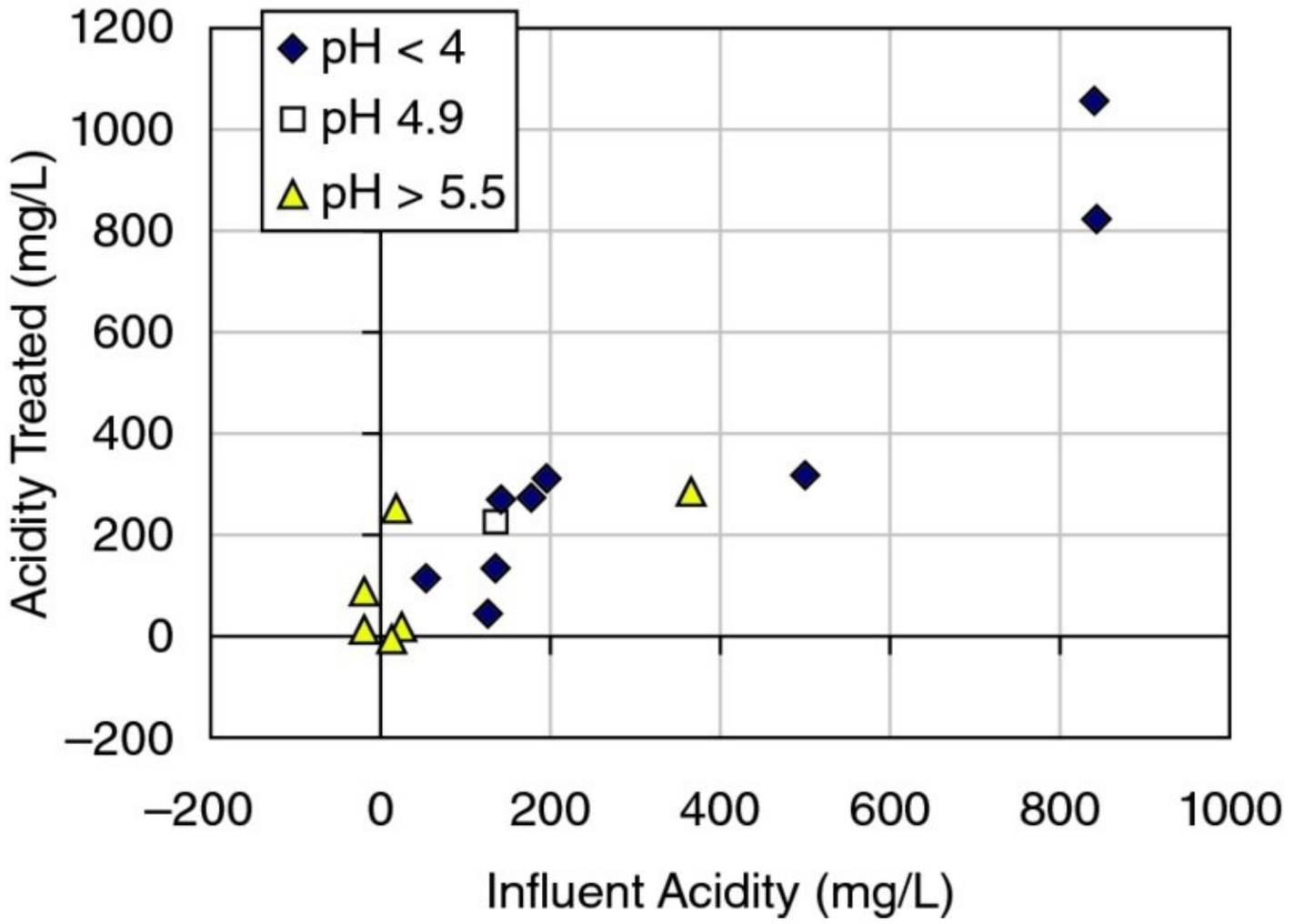

Figure 30.15 Performance of 16 open limestone channels, as documented by Skousen and Ziemkiewicz (), plotted by influent pH.

Vertical-Flow Systems

Vertical-flow wetlands combine the treatment mechanisms of anaerobic wetlands and ALDs in an attempt to compensate for the limitations of both (Hendricks, ; Duddleston et al., ; Kepler and McCleary,). Vertical-flow systems have also been called SAPS (for "successive alkalinity-producing systems"; Kepler and McCleary,) and RAPS (for "reducing and alkalinity-producing systems"; Watzlaf et al., 2000). The basic elements of these systems are similar to those of anaerobic wetlands, but a drainage system is added to force the AMD into direct contact with the alkalinity-producing substrate. The three major system elements are the drainage system, a limestone layer, and an organic layer (Figures 30.16 and 30.17). The system is constructed within a watertight basin, and the drainage system is constructed with a standpipe to control water depths and ensure that the organic and limestone layers remain submerged.

As the AMD waters flow downward through the organic layer, essential functions are performed: dissolved oxygen is removed by aerobic bacteria utilizing biodegradable organic compounds as energy sources, and sulfate-reducing bacteria generate alkalinity and sequester metals as sulfides [reactions (30.1) to (30.4)]. An organic layer capable of lowering dissolved oxygen concentrations to less than 1 mg/L is essential to prevent limestone armoring and for sulfate reduction. In the limestone layer, $CaCO_3$ is dissolved by the acidic, anoxic waters moving down to the drainage system, producing additional alkalinity. The final effluent is discharged into a settling pond for acid neutralization and metal

precipitation prior to ultimate discharge. For influents containing significant quantities of Fe^{3+} and/or sediment, vertical-flow systems should be preceded by either a settling pond or an aerobic wetland so as to limit accumulation of solids on the organic layer surface. For treating highly acidic discharges, several vertical flow cells can be placed in sequence, separated by settling ponds.

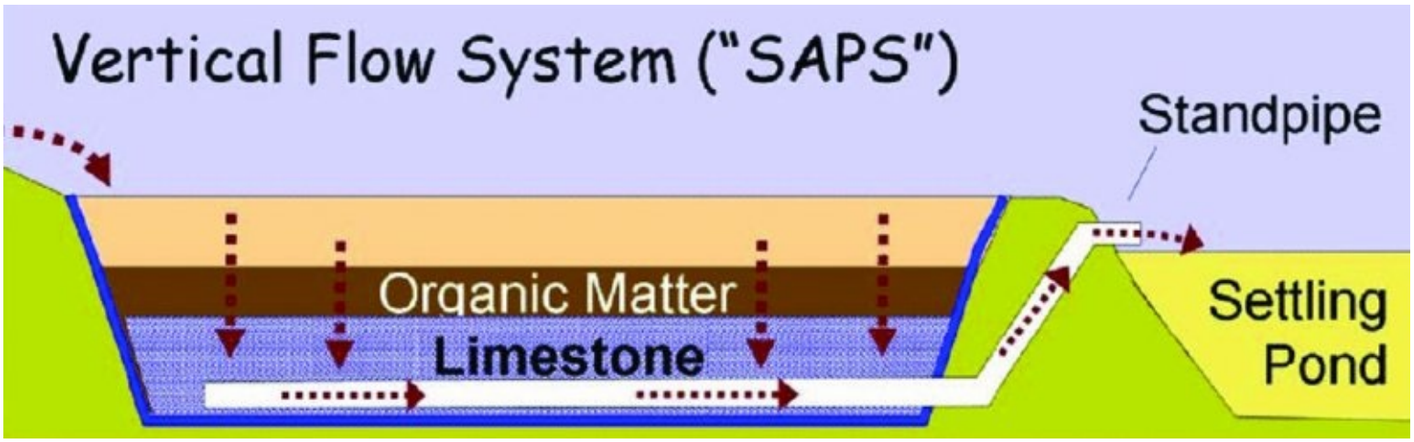

Figure 30.16 Simplified cross-sectional view of a simple vertical-flow treatment system.

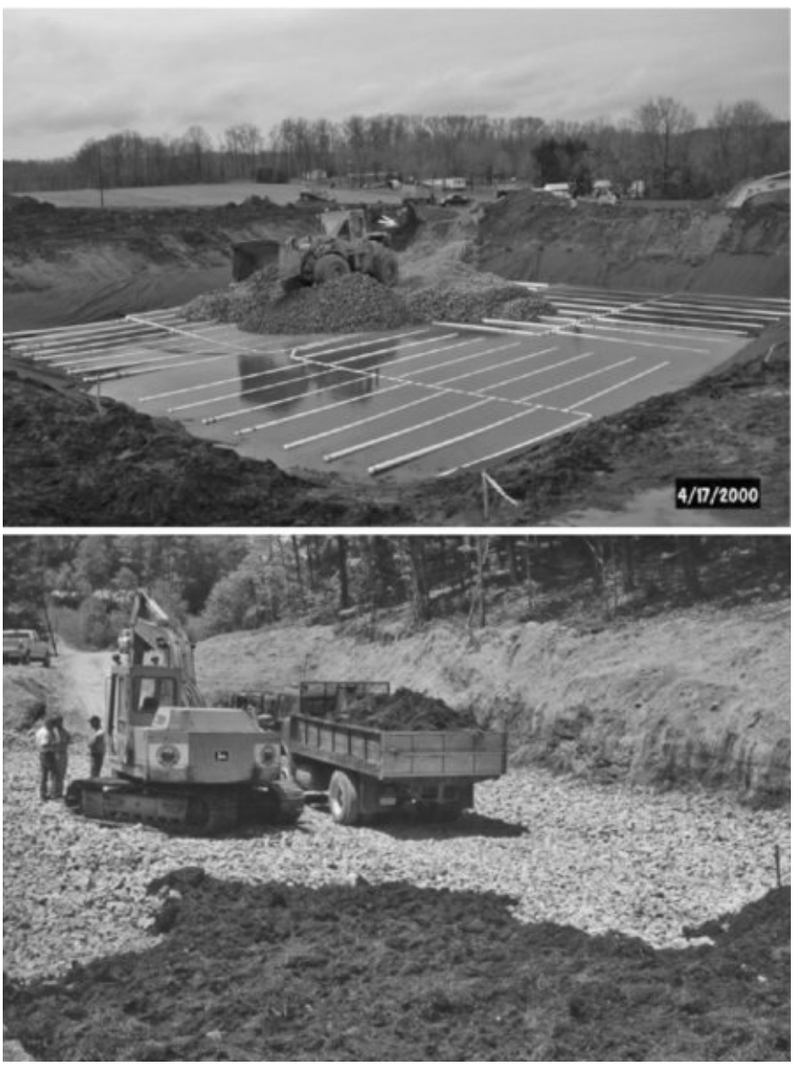

Figure 30.17 Construction of vertical-flow wetlands. A drainage system constructed of perforated plastic piping is placed over a plastic liner.

Water enters the system (Figure 30.16) on the left and must pass vertically through the organic matter and limestone gravel to enter the perforated piping within the limestone layer to exit the system. The drainage system is outfitted by a standpipe that maintains water levels so as to assure that the organic matter and limestone remain submerged. Alkalinity is generated by sulfate reduction and limestone dissolution. Some metals are deposited within the system, but most metal removal occurs via precipitation in the settling pond that receives discharge waters. As shown in Figure 30.17, large limestone gravel (generally, 20 to 30 cm) is placed over the drainage system, and biodegradable but porous organic material is placed over that.

Two major limitations to vertical-flow systems' long-term performance are accumulation of metal floc, primarily Fe and Al in the limestone layer, and degradation of the organic layer. To postpone floc accumulation and eventual clogging, a valved flushing pipe is typically included as part of the drainage system (Kepler and McCleary,). When opened, this drain discharges at a lower elevation than the standpipe (Figure 30.18). Head pressure moves waters through the system rapidly, flushing the gel-like flocs of Al and Fe that tend to accumulate in the drainage pipes and limestone pores. Opening this valve periodically is intended to remove loose floc from the limestone layer, discharging it into the settling pond (Figure 30.19). To assure adequate head pressure for flushing, water depths above the organic layer of 1 to 2 m or greater are generally recommended. However, as demonstrated by Watzlaf et al. (2002), only a small proportion of the total accumulated floc is removed by typical flushing operations. Because floc can be expected to accumulate within the limestone layer, many vertical-flow systems are designed with intricate drainage configurations so as to aid floc removal by the flushing operation.

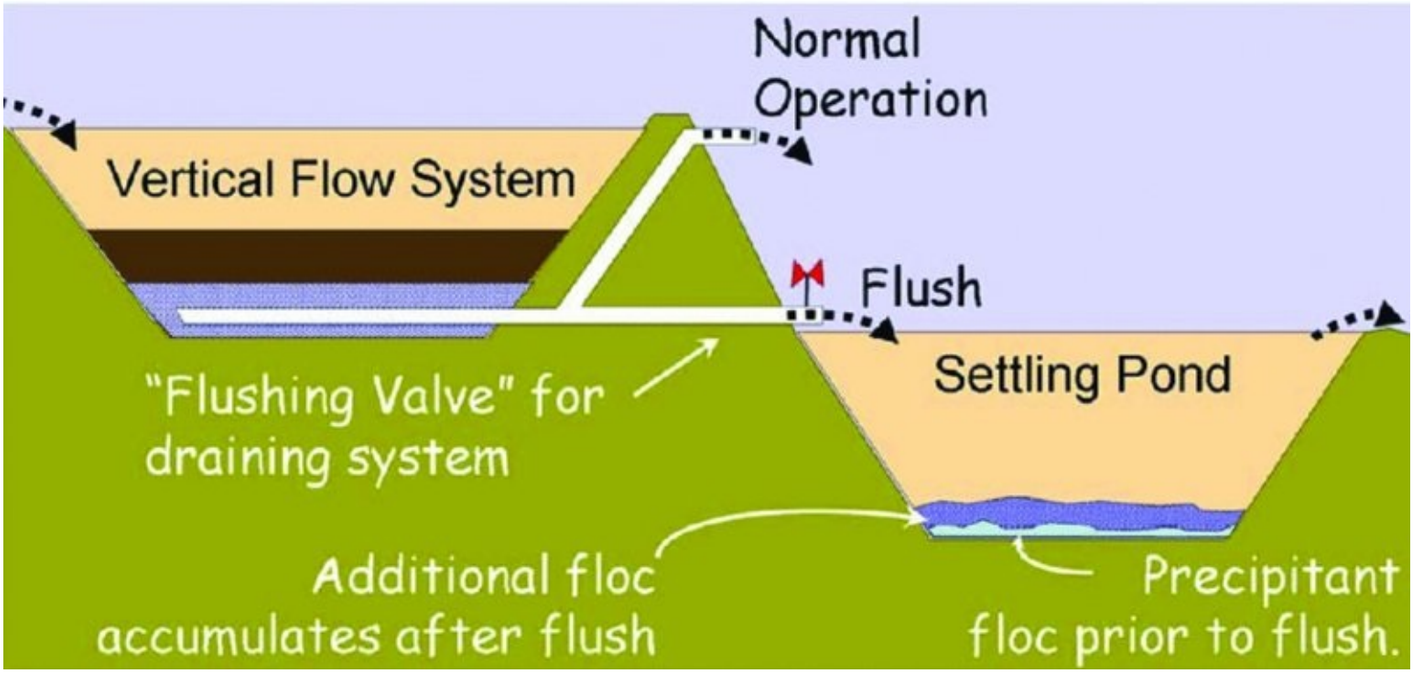

Figure 30.18 An underdrain flushing system can extend the useful lifetime of vertical-flow treatment systems by preventing the accumulation of metal hydroxide floc in the limestone layer.

Figure 30.19 (a) Completed vertical-flow system; (b) operating the flushing system to remove precipitated flocs from the limestone pores.

Generally, systems are built with high-calcium (>90%) limestone in the 10- to 30-cm size range (4 to 6 in.) with a limestone layer thickness in the range 60 to 100 cm. To assure that the volume of limestone is adequate to assure long-term performance, the criteria used to size ALDs [equation (30.8)] can also be used to calculate a volume of limestone.

During normal operation, the system shown in Figure 30.18 discharges through the standpipe. Periodically, floc is removed from the underdrain by opening the flushing valve so that waters can exit rapidly, carrying loose floc into the settling pond. Once the flow ceases, the flushing valve is closed and the system resumes normal operation.

The organic layer is the other major system element that is critical to long-term performance. For the system to operate properly, the organic layer must be sufficiently biodegradable to allow essential functions, but it must also be permeable so that water can move through it into the limestone. Organic functionality can be expected to degrade over time, due to microbial biodegradation and floc accumulation in pore spaces. Materials that have been used successfully include spent mushroom compost, composted manure, and mixtures of composted materials with less-expensive organic sources such as rotting hay. Published design guidelines recommend organic layer depths of 15 to 60 cm. Care should be used in installing the organic layer to assure that the material is well mixed and applied at a uniform depth across the limestone-layer surface. Once the organic layer is in place, any activity causing

compaction or physical disturbance should be avoided to prevent creation of zones of preferential vertical flow that that will “short-circuit” the system and decrease treatment effectiveness (Figure 30.20). The dark blue colors in the figure represent oxidizing conditions occurring more than 45 cm below the organic layer surface, meaning that water is flowing downward rapidly through these areas, while the red colors represent depths of oxidation below 15 cm, meaning that the opposite is occurring; yellows and greens represent intermediate conditions.

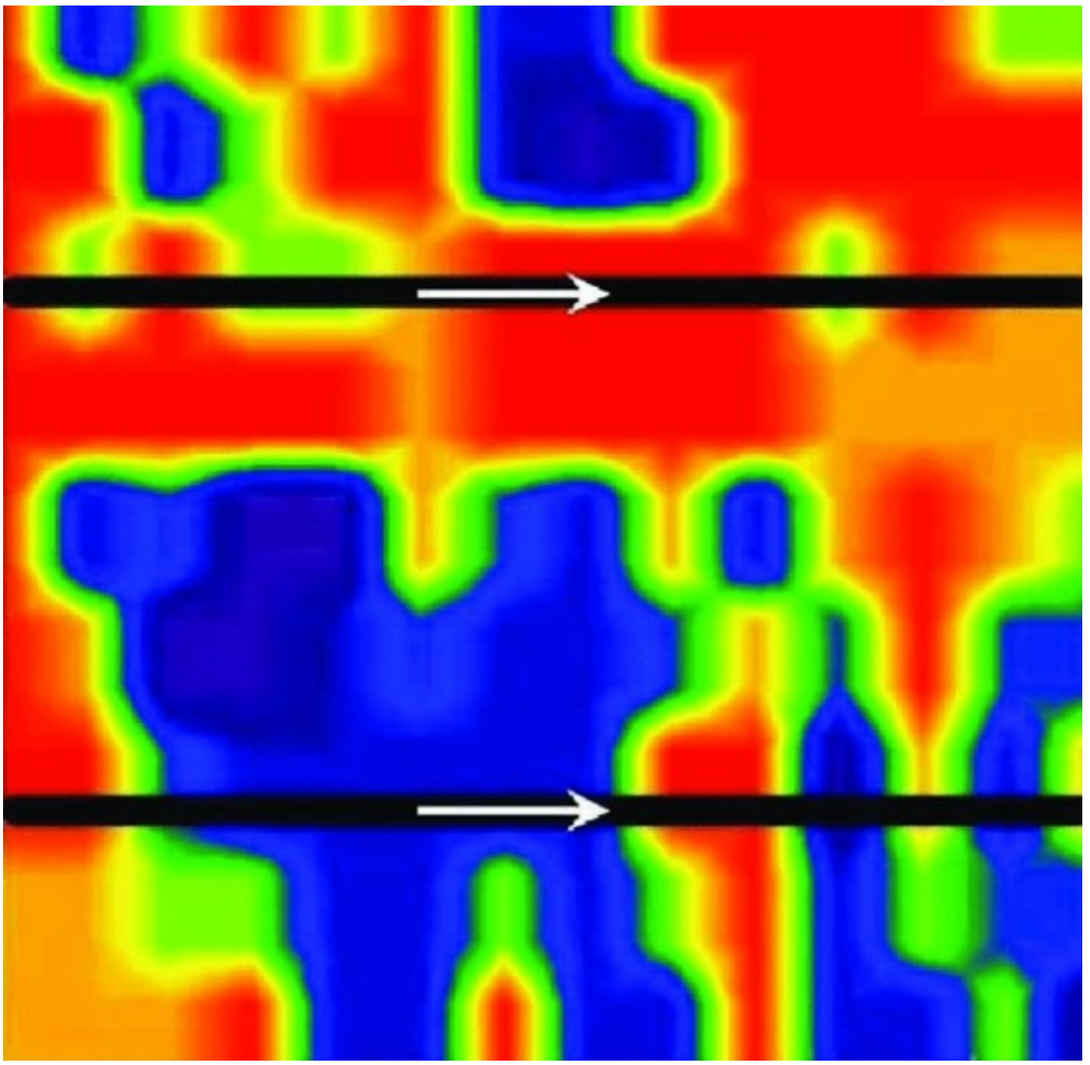

Figure 30.20 Top-view representation of the organic layer and underlying drain configuration (black bars, with arrows representing drainage water flow) of a vertical-flow system in Pennsylvania, with colors representing depth of oxidation. (From Demchak and Skousen, .)

Vertical-flow systems are able to neutralize acidity and promote metal precipitation in difficult treatment situations. Due to the forced contact of the AMD with the limestone, acid neutralization is more rapid in vertical-flow systems than in anaerobic wetlands, so vertical-flow systems generally require shorter residence times and smaller surface areas. Skousen and Ziemkiewicz () describe a system design guideline that sizes vertical-flow systems to treat 20 g/m^2 per day with a 15-h retention time, assuming that the system can attain a 20-year useful life. As a general guideline, Watzlaf et al. (2004) recommend that the initial vertical-flow cell in a sequence can be sized assuming that it will generate 40 to 60 g/m^2 per day of alkalinity and that subsequent cells can be expected to generate 15 to 20 g/m^2 per day. Analysis of performance data gathered by Skousen and Ziemkiewicz () and Jage et al. () demonstrate that influent acidity concentrations and loadings influence performance (Figure 30.21). Of the 33 vertical-flow

systems whose performance was documented by two studies, 19 generated alkalinity at greater than 20 g/m^2 per day and 13 generated alkalinity at greater than 40 g/m^2 per day. Generally, systems receiving higher acid loadings generated more alkalinity than those receiving lower loadings, on both a concentration and a per unit surface area basis.

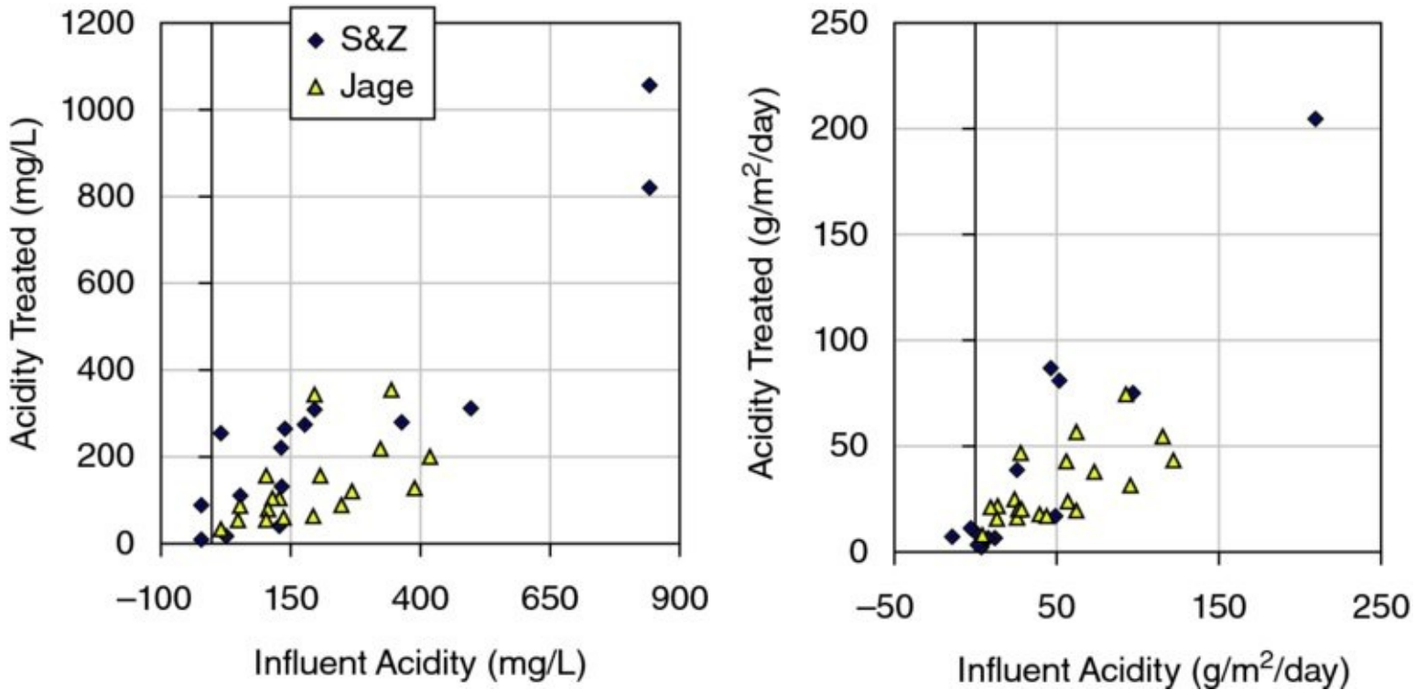

Figure 30.21 Performance data for (a) 18 vertical-flow systems from Jage et al. (), and for (b) 15 vertical-flow systems from Skousen and Ziemkiewicz (). One system point is off-scale in plot (b): (x, y) = (668, 843). Both data sets indicate an influence by influent acidity on system performance.

Sulfate-Reducing Bioreactors

A number of sulfate-reducing bioreactors (SRBs) have been constructed to treat AMD, particularly in low-flow situations, where waters contain high concentrations of metals (western v.s. hardrock mines) (Gusek,). Typically, an SRB is a small version of an anaerobic wetland, but the limestone and compost are mixed or layered in a barrel or small excavation, and water is then introduced so as to maximize anaerobic conditions. Sulfate-reducing bacteria consume organic matter and generate sulfide that can precipitate Fe and other metals as sulfides, and also generate alkalinity that increases pH (Drury,). Some elements, such as Al, may precipitate as hydroxides as the pH increases. Adsorption of metals to organic matter also may be an important contributor to metal removal from water.

A design factor that is critical to SRB effectiveness is the nature of an organic carbon source as it exerts a strong influence on microbial sulfate reduction, which is the dominant alkalinity-generating and metal-complexing mechanism in most SRBs (Neculita et al.,). Ideally, the organic materials are both highly biodegradable and porous, and they are able to remain as such over an extended operating period. Reactors can develop problems with compaction of the substrate, thereby reducing permeability and increasing short-circuiting. Fine-grained organic substrates are particularly vulnerable, and workers have learned to add large strong particles such as gravel, sand, walnut shells, and wood chips to maintain porosity and permeability. Early treatment of SRBs is often poor because the microbial system requires time to adapt to AMD conditions. Inoculation with specialized or previously selected microbial systems sometimes helps to speed up treatment processes.

Other Passive Treatment System Types

The passive treatment systems described above are the most widely used types for acid drainage. Several other types of systems are also available, generally for use in specialized situations. Such methods include limestone ponds, limestone sand beds, limestone diversion wells, and other methods. Several of these other system types are described in the passive treatment design guidelines listed in the References.

Developing a Passive Treatment Strategy

The design of all passive treatment systems starts with characterizations of influent AMD chemistry and flow. Regular sampling over at least a 12-month period is recommended to account for the variations that may occur or in response to seasonal changes or storms. At a minimum, all water samples should be analyzed for pH, total Fe, Mn, Al, SO_4, total alkalinity, and total acidity. Additional analyses, including Fe^{2+}, Fe^{3+}, and dissolved O_2 are necessary if ALD treatment is being considered. If the AMD discharge is intended to achieve regulatory compliance, sampling personnel should assure that worst-case conditions, however defined, are represented by the sampling data.

The selection of a passive treatment system is governed by both influent water quality and site characteristics. Figure 30.1 illustrates a decision process for selecting an appropriate system for a given discharge. For net alkaline discharges containing elevated concentrations of Fe, no additional alkalinity additions are needed. The only conditions necessary to complete treatment are an oxidizing environment and sufficient residence time to allow for metal oxidation and precipitation. These conditions can be provided by a settling pond and, if a sufficiently large area is available, the settling pond may be followed by an aerobic wetland for effluent polishing (more complete removal of settleable contaminants).

The treatment of net acidic drainage can be handled in a number of ways, depending on the influent chemistry. If the influent quality is suitable for an ALD, an ALD can be employed as a pretreatment method. A post-ALD settling pond or aerobic wetland is required to allow for the oxidation and precipitation of metals. Acidic waters that are not suitable for ALDs can be treated with either an anaerobic wetland or a vertical-flow system. Due to the potentially large demands on land area of anaerobic wetlands, they are usually practical only for low-flow situations. For systems that receive water that has a pH above 4, settling ponds may precede an anaerobic wetland cell to remove significant quantities of Fe. The remaining discharges can be treated using a vertical-flow system. Where terrain is suitable, an open limestone channel can be used to carry the treatment waters while adding additional alkalinity in the process.

Another factor governing system selection will be the cost of available treatment options. Skousen and Ziemkiewicz () have documented cost-effectiveness for a number of different passive system installations by estimating construction costs from system dimensions, assuming 20-year lifetimes, and calculating the cost per ton of acid neutralization using measured performance data. Per-unit acidity treatment costs vary dramatically for all system types. In general, anoxic limestone drains render the most cost-effective passive treatment, while open limestone channels were also able to render treatment that was less costly on average than either type of wetland system and vertical-flow systems. Of course, ALDs have very specific influent water quality requirements and are not an option for many AMD discharges, while OLCs can operate only within water conveyances. Generally speaking, the systems that are able to treat the most problematic waters—highly acidic and oxidized—are also the most costly.

Conclusions

Passive treatment systems can be a component of an AMD treatment strategy. They can function as either stand-alone treatment strategies or as pretreatment to reduce the cost of active treatment. Passive treatment system performance varies significantly among constructed systems, due to differences in site conditions. One factor that influences the performance of systems that utilize limestone is influent acidity, as systems receiving higher acidity are often able to neutralize acidity more effectively. Passive treatment systems are effective at renovating waters with low pH, high acidity, and high concentrations of acid-soluble metals, including Fe and Al, but their effectiveness at removing Mn is generally limited unless large treatment areas are available.

Problems and Questions

The costs for building the systems in these problems can be estimated by figuring the volumes and sizes of ponds, trenches, and so on. Estimate the excavation costs at $\$22/yd^3$. Limestone is \$27/ton and 2 tons of limestone occupies 1 yd^3 of volume. Organic matter is \$55/ton and organic matter is 1 ton/yd^3 of volume.

1. The Deer Meadow mine site near Wheeling, West Virginia is on nearly level topography by a historically famous trout stream, Three Horse Creek. Trout are no longer found in the creek, and a local environmental group is pressuring the operator to restore the creek as part of the mine development program permit. As part of the development permit, the operator drilled a shallow borehole in the proposed mine area to show the groundwater characteristics before mining. The groundwater aquifer is confined, and the groundwater comes to the surface with the following characteristics:

Flow:	100 gal/min
Acidity:	120 mg/L as $CaCO_3$
pH:	3.0
Iron:	20 mg/L, 50% is ferric
Manganese:	11 mg/L
Aluminum:	12 mg/L
Dissolved oxygen:	2 to 3 mg/L

   Select and design a passive treatment system for this site to reduce the metal and acidity concentrations in the water before discharge into Three Horse Creek. The water from the borehole comes to the surface about 2500 ft from the stream down a gentle incline of about 2% slope. What materials, and how much of each material, would you need to build the passive system? Prepare diagrams (map view and cross section) of the system and state how much the passive system would cost to build based on information given.

2. In Williamson County in southern Illinois, a small groundwater seep from a surface coal mine dug into the Danville coal continues to plague an operator who cannot get his bond released. He has been treating the seep with a small sodium hydroxide (NaOH) drip system at a cost of about \$20,000 per year. He heard that building a passive treatment system would really reduce his AMD treatment costs. The water has the following characteristics:

Flow:	50 gal/min

Acidity:	250 mg/L as $CaCO_3$
pH:	3.1
Iron:	15 mg/L, all is ferric
Manganese:	25 mg/L
Aluminum:	35 mg/L
Dissolved oxygen:	8 mg/L

Select, design, draw (map view and cross section), and provide an estimate for a passive system for treating this water.

3. In Harlan County, Kentucky, the Middle Princess No. 9 coal bed is the source of AMD at various rates from the main mine shaft. To increase tourism to the area, the local redevelopment agency wants to treat the water as part of the reclamation of the site and of the prized bass fishing lake into which the stream empties. The mine needs a design for a passive treatment system that can be installed. The agency has a grant to pay $10,000 to design this passive system. The water has the following characteristics:

Flow:	150 gal/min
Acidity:	1250 mg/L as $CaCO_3$
pH:	3.4
Iron:	315 mg/L, all ferrous
Manganese:	25 mg/L
Aluminum:	45 mg/L
Dissolved oxygen:	<0.9 mg/L

Select the appropriate system, draw a sketch of the system, tell exactly what they need to build the system, and estimate costs for construction.

Acknowledgment

Parts of this chapter were published as Virginia Cooperative Extension Publication 460-133 (Zipper et al., 2010).

References and Suggested Reading

Passive Treatment Design Guidelines

Caterpillar, Inc., 1997. Caterpillar Performance Handbook. Caterpillar, Peoria, IL.

Hedin, R.S., 2002. Passive treatment of polluted mine waters. In: Mine Water: Hydrology, Pollution, Remediation, P.L. Younger, S. Banwart, and R.S. Hedin, eds. Kluwer Academic, Norwell, MA, Chap. 5.

Hedin, R.S., Nairn, R.W., and Kleinmann, R.L.P., 1994. Passive Treatment of Coal Mine Drainage. Information Circular IC9389. U.S. Department of the Interior, Bureau of Mines, Washington, DC.

Skousen, J., 1996. Overview of Passive Systems for Treating Acid Mine Drainage. West Virginia

University Extension Service. http://www.wvu.edu/~agexten/landrec/passtrt/passtrt.htm.

Skousen, J., Sexstone, A., and Ziemkiewicz, P., 2000. Acid mine drainage treatment and control. In: Reclamation of Drastically Disturbed Lands, R. Barnhisel, W. Daniels, and R. Darmody, eds. American Society of Agronomy, Madison, WI, pp. 131–168.

Skovran G.A., and Clouser, C.R., 1998. Design considerations and construction techniques for successive alkalinity producing systems. In: Proceedings of the 1998 Annual Meeting of the American Society for Surface Mining and Reclamation, St. Louis, MO, May 16–21.

Other General References and Suggested Reading

Brooks, R., Samuel, D.E., and Hill, J.B., 1985. Wetlands and Water Management on Mined Lands: Proceedings of a Conference. Pennsylvania State University, University Park, PA.

Demchak, J., and Skousen, J., 2000. Treatment of Acid Mine Drainage by Four Vertical Flow Wetlands in Pennsylvania. West Virginia University Cooperative Extension Service. http://www.wvu.edu/~agexten/landrec/treatment.htm.

Drury, W.J., 2000. Modeling of sulfate reduction in anaerobic solid substrate bioreactors for mine drainage treatment. Mine Water Environment, vol. 19, pp. 18–28.

Duddleston, K.N., Fritz, E., Hendricks, A.C., and Roddenberry, K., 1992. Anoxic cattail wetland for treatment of water associated with coal mining activities. In: Proceedings of the 1992 Annual Meeting of the American Society for Surface Mining and Reclamation, Duluth, MN, June 15–18, pp. 249–254.

Faulkner, B.B., and Skousen, J.G., 1994. Treatment of acid mine drainage by passive treatment systems. In: Proceedings of the International Land Reclamation and Mine Drainage Conference, Pittsburgh, PA, April 24–29. Special Publication 06A-94. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 250–257.

Gusek, J.J., 2004. Scaling up design challenges for large scale sulfate reducing bioreactors. In: Proceedings of the American Society of Mining and Reclamation and West Virginia Surface Mine Drainage Task Force, Morgantown, WV, pp. 752–765.

Hedin, R.S., and Watzlaf, G.R., 1994. The effects of anoxic limestone drains on mine water chemistry. In: Proceedings of the International Land Reclamation and Mine Drainage Conference, Pittsburgh, PA, April 24–29, pp. 185–194.

Hedin, R.S., Watzlaf, G.R., and Nairn, R.W., 1994. Passive treatment of acid mine drainage with limestone. Journal of Environmental Quality, vol. 23, pp. 1338–1345.

Hendricks, A.C., 1991. The use of an artificial wetland to treat acid mine drainage. In: Proceedings of the International Conference on the Abatement of Acidic Drainage, Montreal, QC, Canada, September.

Huntsman, B.E., Solch, J.B., and Porter, M.D., 1978. Utilization of a *Sphagnum* species dominated bog for coal acid mine drainage abatement. Abstracts, 91st Annual Meeting of the Geologic Society of America, Ottawa, ON, Canada.

Hyman, D.M., and Watzlaf, G.R., 1995. Mine drainage characterization for the successful design and evaluation of passive treatment systems. In: Proceedings of the 17th Annual Conference of the National

Association of Abandoned Mine Lands, French Lick, IN, October.

Jage, C., Zipper, C.E., and Noble, R., 2001. Factors affecting alkalinity generation by successive alkalinity producing systems: regression analysis. Journal of Environmental Quality, vol. 30, pp. 1015–1022.

Kepler, D.A., and McCleary, E.C., 1994. Successive alkalinity-producing systems (SAPS) for the treatment of acidic mine drainage. In: Proceedings of the International Land Reclamation and Mine Drainage Conference, Pittsburgh, PA, April 24–29, pp. 195–204.

Kepler, D.A., and McCleary, E.C., 1997. Passive aluminum treatment successes. In: Proceedings of the National Association of Abandoned Mine Lands Programs, Davis, WV, August 17–20.

Kirby, C., and Cravotta, C., 2005. Net alkalinity and net acidity: I. Theoretical considerations, and II. Practical considerations. Applied Geochemistry, vol. 20, pp. 1920–1964.

Neculita, C.-M., Zagury, G.J., and Bussière, B., 2007. Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria: critical review and research needs. Journal of Environmental Quality, vol. 36, pp. 1–16.

Rose, W.A., 2006. Long-term performance of vertical flow ponds: an update. In: Proceedings of the 7th International Conference on Acid Rock Drainage, St. Louis, MO, pp. 1704–1716.

Samuel, D.E., Sencindiver, J.C., and Rauch, H.W., 1988. Water and soil parameters affecting growth of cattails. In: Proceedings, Mine Drainage and Surface Mine Reclamation, Pittsburgh, PA, April 19–21, vol. 1. Information Circular 9183. U.S. Department of the Interior, Bureau of Mines, Washington, DC, pp. 367–374.

Skousen, J.G., and Ziemkiewicz, P.F., 1996. Acid Mine Drainage Control and Treatment, 2nd ed. National Mine Land Reclamation Center and West Virginia University, Morgantown, WV, 254 pp.

Skousen, J., and Ziemkiewicz, P., 2005. Performance of 116 passive treatment systems for acid mine drainage. In: Proceedings of the National Meeting of the American Society of Mining and Reclamation.

Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., and Hellier, W., 1999. Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage. Acid Drainage Technology Initiative (ADTI) of the U.S. Office of Surface Mining. Published by the National Mine Land Reclamation Center, West Virginia University, Morgantown, WV.

Skousen, J.G., Sexstone, A.J., and Ziemkiewicz, P.F., 2000. Acid mine drainage control and treatment. In: Reclamation of Drastically Disturbed Lands. Agronomy No. 41. American Society of Agronomy and American Society for Surface Mining and Reclamation, Madison, WI, Chapter 6.

Watzlaf, G.R., 2004. Treatment of high-flow, low-iron mine drainage with a semi-passive system. In: Proceedings of the National Meeting of the American Society for Surface Mining and Reclamation, Morgantown, WV, pp. 1962–1973.

Watzlaf, G., Schroder, K., and Kairies, C., 2000. Long-term performance of anoxic limestone drains. Mine Water and the Environment, vol. 19, pp. 98–110.

Watzlaf, G.R., Kairies, C.L., and Schroeder, K.T., 2002. Quantitative results from the flushing of four reducing and alkalinity-producing systems. In: Proceedings of the 23rd West Virginia Surface Mine

Drainage Task Force Symposium, Morgantown, WV.

Watzlaf, G.R., Schroeder, K.T., Kleinmann, R.L., Kairies, C.L., and Nairn, R.W., 2004. The Passive Treatment of Coal Mine Drainage. USDOE/NETL Report 2004/1202. U.S. Department of Energy, Washington, DC, 72 pp.

Wieder, R.K., and Lang, G.E., 1982. Modification of acid mine drainage in a freshwater wetland. In: Proceedings of the Symposium on Wetlands of the Unglaciated Appalachian Region, Morgantown, WV, pp. 43–53.

Ziemkiewicz, P., Skousen, J., Brant, D., Sterner, P., and Lovett, R.J., 1997. Acid mine drainage treatment with armored limestone in open channels. Journal of Environmental Quality, vol. 26, pp. 1017–1024.

Zipper, C.E., and Skousen, J.G., 2010. Influent water quality affects performance of passive treatment systems for acid mine drainage. Mine Water and the Environment, vol. 29, pp. 135–143.

Zipper, C.E., and Skousen, J., 2010. Influent water quality affects performance of passive treatment systems for acid mine drainage. Mine Water and the Environment, vol. 29, pp. 135–143.

Zipper, C., Skousen, J., and Jage, C., 2010. Passive treatment of acid-mine drainage. Reclamation Guidelines for Surface Mined Lands. Virginia Cooperative Extension Publication 460-133. Powell River Project, Blacksburg, VA.

31
THE IRON MOUNTAIN MINE IN SHASTA COUNTY, CALIFORNIA

JAMES A. JACOBS AND STEPHEN M. TESTA

The Iron Mountain mine is the most infamous example of what happens when iron sulfide–rich ores are disturbed and exposed during mining operations. Located 9 miles northwest of the city of Redding in Shasta County, California, the Iron Mountain mine is located near the pristine beauty of Mt. Shasta, a local tourist destination. The mine is also in a critical area where millions rely on the nearby reservoirs and rivers for drinking and irrigation water supplies. The mines at Iron Mountain have long been abandoned, but the acid drainage continues and is being addressed in a heavily regulated environmental remedial action.

Introduction

Iron Mountain is a massive sulfide deposit, formed 350 to 400 million years ago in an island-arc setting in a marine environment as a result of geothermal hot springs on the sea floor expelling sulfur-rich hydrothermal fluids (U.S. Environmental Protection Agency, 2006). From the 1860s through 1963, the 4400-acre Iron Mountain mine site was mined periodically for iron, silver, gold, copper, zinc, and pyrite. Figure 31.1 shows the historic mine. Although mining operations were discontinued in 1963, underground mine workings, waste rock dumps, piles of mine tailings, and an open mine pit remain at the site. Historic mining activity at the mine has disturbed pyrite-rich rocks, exposing the iron sulfide minerals to surface water, rainwater, and oxygen. Sulfuric acid is generated when iron sulfide rocks are exposed to oxygen and moisture catalyzed by iron- and sulfide-oxidizing bacteria, which are ubiquitous in these rocks. Figure 31.2 shows the location maps for the Iron Mountain mine.

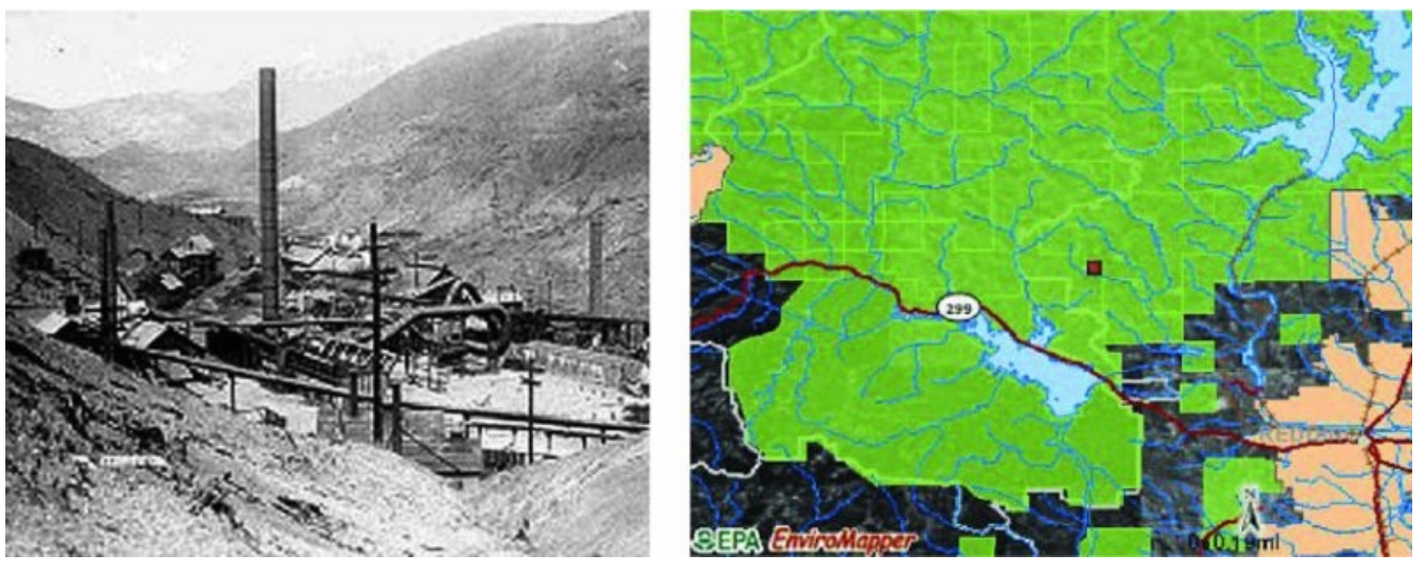

FIGURE 31.1 Iron Mountain Mine was famous for being the most productive copper mine in California as well as one of the largest in the world. (From U.S. Environmental Protection Agency, 2006.)

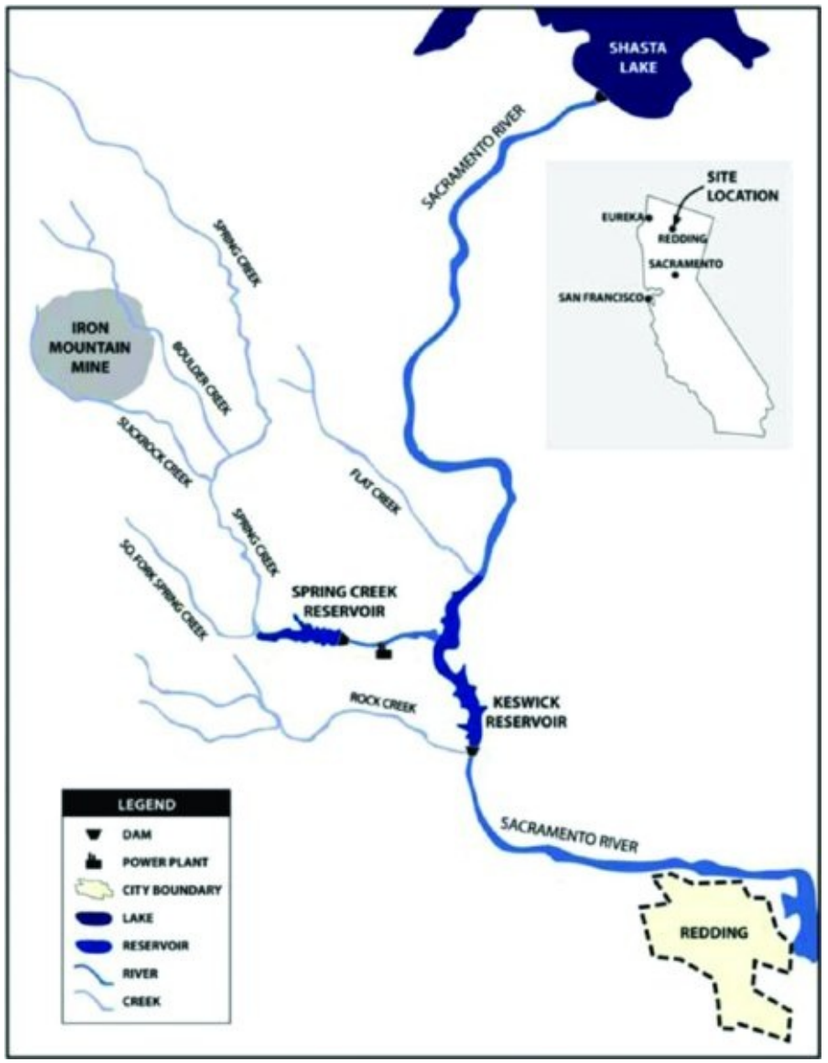

FIGURE 31.2 Detailed site area map of the Iron Mountain mine. (From U.S. Environmental Protection Agency, 2006.)

The Richmond mine of the Iron Mountain copper deposit contains some of the most acid mine waters ever reported, with pH measured as low as −3.6. The Richmond mine also has combined metal concentrations as high as 200 g/L and sulfate concentrations as high as 760 g/L (Nordstrom and Alpers, 1999). The sulfuric acid produced runs through the mountain and leaches out copper, cadmium, zinc, and other heavy metals. This acid drainage flows out of the seeps and portals of the mine. Much of the acidic mine drainage is ultimately channeled into the Spring Creek Reservoir by creeks surrounding the Iron Mountain mine (Figure 31.2). The Bureau of Reclamation periodically releases the stored acid mine drainage into Keswick Reservoir. Planned releases are timed to coincide with the presence of diluting releases of water from Shasta Dam (U.S. Environmental Protection Agency, 2010, 2011).

Geochemistry of Iron Mountain

The biogeochemistry at the Richmond mine at Iron Mountain has been studied and described in detail by Alpers et al. (1992, 1994), Nordstrom and Alpers (1999), and Robbins et al. (2000). Studies of extreme acid drainage from the Iron Mountain massive sulfide deposit and associated heavy metal discharges were also evaluated and reported by Alpers et al. (2003). The heavy metal discharges into nearby drainages and reservoirs were documented by Nordstrom et al. (1977, 1999, 2000). Underground at the

Richmond mine, extremely acidic mine waters with pH values as low as −3.6, total dissolved metal concentrations as high as 200 g/L, and sulfate concentrations as high as 760 g/L have been documented by Nordstrom et al. (2000). The work of Baker, Banfield, and others (2003, 2004, 2009), also at the Richmond mine, has been instrumental in an understanding of the complex interactions of various microbial populations in acidophilic microbial communities in extreme acid conditions.

Due to the extreme acidic conditions, the Richmond mine has also been the location and identification of unusual acidophilic mine-dwelling biofilm communities as well as specific organisms, including ultra-small, one-celled acidophilic microbes. The ultra-small acidophilic archaea have been viewed using a cryoelectron microscope to obtain high-resolution, three-dimensional images. The microbes have been identified as archaeal Richmond mine acidophilic nanoorganisms, which are only 200 to 400 nm in diameter (Baker et al., 2010).

Figure 31.3 shows the hydrologic model for Iron Mountain. The gossan outcrop at the peak of Iron Mountain shows a natural weathering of sulfide deposits which is an indicator that mines in the same geologic units may generate acid drainage (Figure 31.4).

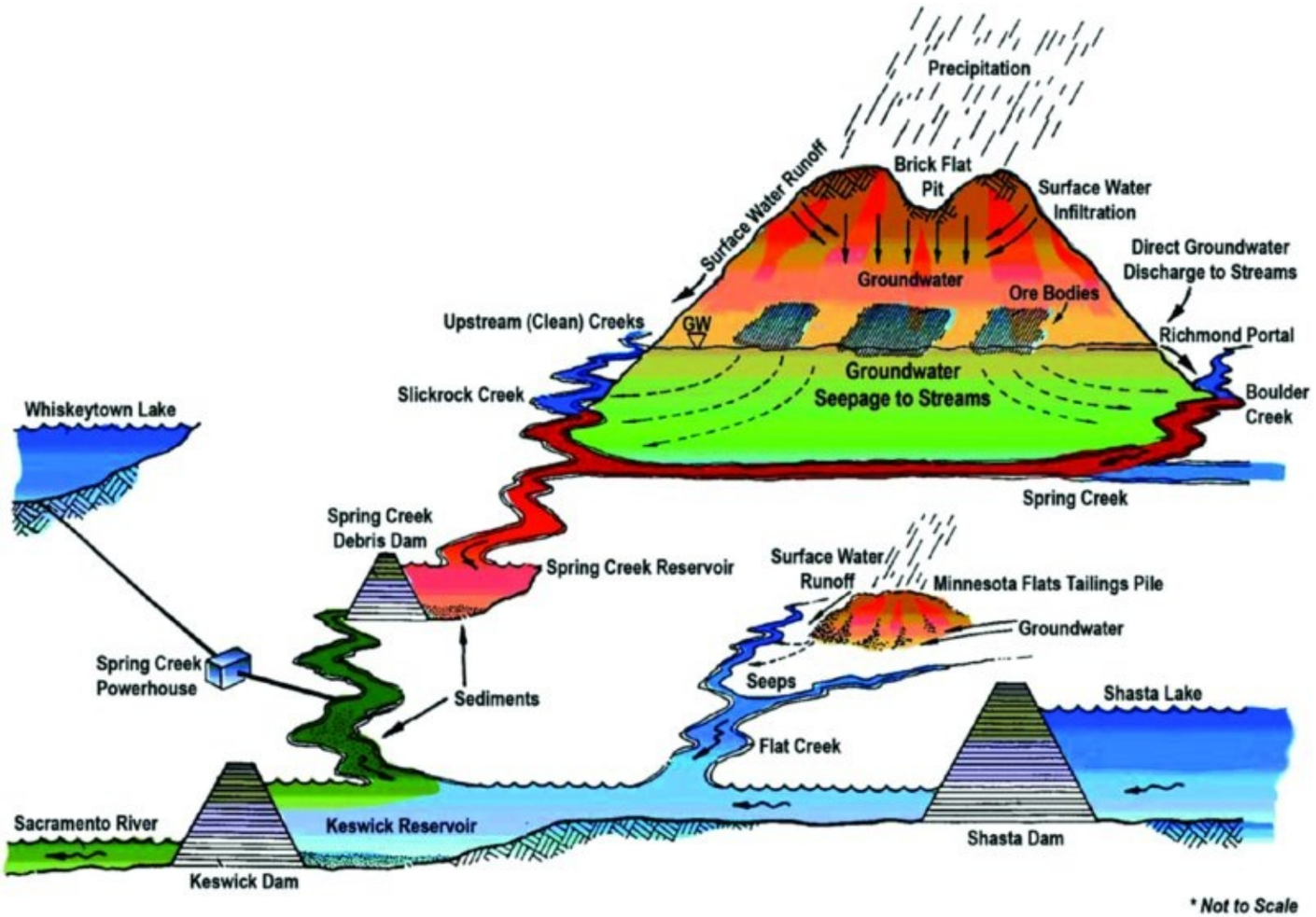

DIAGRAM OF ACID MINE DRAINAGE AT IRON MOUNTAIN MINE

FIGURE 31.3 Iron Mountain Mine hydrologic site conceptual model showing the migration of water through the mountain. (From U.S. Environmental Protection Agency, 2006.)

FIGURE 31.4 Gossan, the rust-colored, oxidized iron ore, outcrops near the summit of Iron Mountain where sulfide deposits are 95% pyrite. (From U.S. Environmental Protection Agency, 2006.)

Remedial Actions

The environmental issues at the Iron Mountain mine site are being addressed in six stages, including the initial emergency actions and five long-term remedial phases focusing on water management and cleanup of major contaminant sources in Boulder Creek, the Old mine/No. 8 mine, area source acid mine discharges drainage and sediments.

Emergency Actions

A lime neutralization process facility was installed at Iron Mountain to treat acid mine discharge from the Richmond Portal prior to discharge to the reservoir. The system was first operated by the U.S. Environmental Protection Agency (EPA) during the winter rainy season of 1988 until 1989. Rhône-Poulenc, Inc., operated a similar system from 1989 to 1994.

Water Management

In late 1986, the EPA selected cleanup remedies addressing several parts of the water management area. Cleanup activities include capping selected cracked and caved ground areas, diverting clean Upper Slickrock Creek water around waste rock and mine tailing piles, diverting Upper Spring Creek, diverting clean surface water in South Fork Spring Creek to Rock Creek, enlarging the Spring Creek debris dam,

and performing hydrogeological studies and field-scale pilot demonstrations to better define the feasibility of controlling acid mine drainage formation. The studies and pilot demonstrations were completed. In 1989, the EPA completed capping cracked and caved ground areas and the open-pit mine on Iron Mountain. The EPA completed the diversion of Slick Rock Creek in early 1990. Rhône-Poulenc completed construction of the Upper Spring Creek diversion project in early 1991.

Legal Settlement

After years of legal battles, a settlement was reached in the case of the *United States* v. *Iron Mountain Mines, Inc., et al.*, DOJ Ref. 90-11-3-196A. The case was settled by the U.S. EPA and the state of California with the responsible parties. Under the proposed consent decree, the settling parties agreed to a $862 million settlement to pay for the Iron Mountain cleanup costs (U.S. Environmental Protection Agency, 2000). The estimated capital costs for 2012 included about $200 million for equipment and treatment facilities as well as an annual operations and maintenance budget of about $5 to $7 million.

The EPA has not implemented two of the proposed projects, the South Fork Spring Creek Diversion and the enlargement of the Spring Creek Debris Dam. The EPA has proposed an alternative treatment approach that eliminated the need for these water management actions (U.S. Environmental Protection Agency, 2010, 2011).

Richmond Mine and Lawson Tunnel Acid Mine Drainage Discharges

The EPA completed its study of the major point-source contaminant sources in the Boulder Creek Watershed. In late 1992, the EPA selected an interim remedy to treat the acid mine drainage discharges from the Richmond mine and Lawson tunnel by constructing collection and conveyance systems and a lime neutralization treatment plant. The treatment plant has been built and has been operating since 1994. Treatment will continue until an alternative remedy can be developed to recover metals or control the discharges to ensure meeting all cleanup goals. As part of the neutralization process, large volumes of sludge are generated, which are then stored on site.

Old Mine/No. 8 Mine Acid Mine Drainage Discharges

The EPA has studied the nature and extent of contamination which discharges from the mine seep that originates from the Old mine and the No. 8 mine. In the fall of 1993, the EPA selected an interim cleanup remedy, which included collecting and treating the acid mine drainage discharges from these sources. Since 1994, a collection and conveyance system and a treatment system have been built and have been in operation to treat these acid mine drainage discharges.

Slickrock Creek Area Source Acid Mine Drainage Discharges

The EPA completed its study of the nature and extent of the area source acid mine drainage discharges from the Slickrock Creek drainage at the Iron Mountain mine. The EPA selected a remedy that relies on the collection and treatment of the contaminated Slickrock Creek flows to establish significant additional control of the Iron Mountain mine acid mine drainage discharges in September 1997. By September 2000 the EPA completed the construction of a clean water diversion system, a 5-acre sedimentation basin, surface water controls, a small earthfill embankment dam, and a conveyance pipeline to ensure the collection and treatment of the contaminated discharges at the existing treatment plant. Only minor modifications to the Iron Mountain mine treatment plant were required to implement this additional treatment effort (U.S. Environmental Protection Agency, 2010, 2011).

Spring Creek Arm of Keswick Reservoir Sediments

The EPA completed its study of the nature and extent of contamination associated with sediments downgradient of Iron Mountain mine that are located in the Spring Creek Arm of Keswick Reservoir. In September 2000, the EPA selected a remedy that provides for dredging approximately 200,000 yd^3 of copper- and zinc-contaminated sediments from the Spring Creek Arm of Keswick Reservoir. The EPA initiated construction of the first phase of this cleanup action by constructing access roadways and clearing the disposal cell area in August 2008. The EPA expects to complete construction of the project infrastructure and perform the contaminated sediment dredging operations over the next three to four years.

Boulder Creek Area Source Acid Mine Drainage Discharges

The EPA continues to collect data to characterize the nature and extent of Boulder Creek area source acid mine drainage discharges. The EPA is continuing to study potential remedial approaches for the area source acid mine drainage discharges from the Boulder Creek drainage.

Remedial Performance

The installation and operation of the full-scale neutralization system, the capping of areas of the mine, and the construction and operation of the Slickrock Creek Retention Reservoir to collect contaminated runoff for treatment have significantly reduced the acid and metal contamination in surface water at the Iron Mountain mine site. Cleanup activities are continuing, and additional studies are taking place. The diversion of Upper Spring Creek has greatly increased the ability of the EPA and the Bureau of Reclamation to manage the continuing release of contaminants from the site to minimize harm to the Sacramento River ecosystem until a final remedy can be selected and implemented (U.S. Environmental Protection Agency, 2010, 2011).

In September 1983, Iron Mountain mine was placed on the list of the nation's most hazardous waste sites, known as the Superfund National Priorities List. Since that time the EPA has studied the sources of the acid mine drainage and has carried out several emergency response and long-term cleanup actions to reduce the acid mine drainage entering the Sacramento River ecosystem. The EPA collects acid mine drainage from all the underground mines and area-wide sources in Slickrock Creek and treats the acid mine drainage in a lime neutralization treatment plant. After completing the Slickrock Creek Retention Reservoir in 2004 to collect acid mine drainage discharges from the Slickrock Creek watershed for treatment, the EPA now prevents 98% of metals from the entire mine property from entering the Sacramento River. Treating acid drainage with lime and other neutralizing agents creates a gypsum waste product that must be stored on site in a disposal area. Given the large volumes of waste sludge generated on an annual basis, the capacity of the disposal area for the sludge will reach capacity in 2030. New technologies might be able to recycle some of the resources, including the high-strength sulfuric acid, dissolved metals, and the water. Research is needed to develop new technologies.

Regulatory Challenges

In 1989, the EPA ordered the potentially responsible parties to implement emergency response corrective measures to remove the metal contamination. In 1990, the EPA, under an administrative order, required the parties to implement the Upper Spring Creek diversion cleanup action. In 1991, the EPA ordered the potentially responsible parties to assume responsibility for the operation and maintenance of completed

cleanup actions. In 1992, the EPA ordered the potentially responsible parties to construct the treatment system for the Boulder Creek Watershed. In 1993, the EPA ordered potentially responsible parties to implement the collection and treatment system for the acid mine drainage discharges at the Old mine/No. 8 mine (U.S. Environmental Protection Agency, 2010, 2011).

Resource Recovery

Iron Mountain Mine and mines with similar biogeochemical conditions that generate significant acid drainage and prior to treatment, threatened groundwater and surface water, are also sites where economic recovery of metals, sulfur, water or other resources is worth considering. Many factors affect economic viability of sustainable recovery projects. New technologies for resource recovery are being developed. Pending favorable prices for recovered resources, sites like Iron Mountain may offset some or all of their long-term treatment costs with sustainable resource recovery projects.

References and Suggested Reading

Alpers, C.N., Nordstrom, D.K., and Burchard, J.M., 1992. Compilation and Interpretation of Water-Quality and Discharge Data for Acidic Mine Waters at Iron Mountain, Shasta County, California, 1940–91. Water-Resources Investigation Report 91-4160. U.S. Geological Survey, Reston VA.

Alpers, C.N., Nordstrom, D.K., and Thompson, J.M., 1994. Seasonal variations of Zn/Cu ratios in acid mine water from Iron Mountain, California. In: Environmental Geochemistry of Sulfide Oxidation, C.N. Alpers and D.W. Blowes, eds. ACS Sympasium Series 550. American Chemical Society, Washington, DC, pp. 324–344.

Alpers, C.N., Nordstrom, D.K., and Spitzley, J., 2003. Extreme acid mine drainage from a massive sulfide deposit: the Iron Mountain end-member. In: Environmental Aspects of Mine Wastes, J.L. Jambor, D.L. Blowes, and A. I. M. Ritchie eds. Mineralogy Association of Canada Short Course Series 31, pp. 407–430.

Baker, B.J., and Banfield, J.F., 2003. Microbial communities in acid mine drainage. FEMS Microbiology Ecology, vol. 44, pp. 139–152.

Baker, B.J., Lutz, M.A., Dawson, S.C., Bond, P.L., and Banfield, J.F., 2004. Metabolically active eukaryotic communities in extremely acidic mine drainage. Applied and Environmental Microbiology, vol. 70, no. 10, pp. 6264–6271.

Baker, B., Tyson, G., Goosherst, L., and Banfield, J., 2009. Insights into the diversity of eukaryotes in acid mine drainage biofilm communities. Applied and Environmental Microbiology vol. 75, no. 7, p. 2192.

Baker, B.J., Comolli, L.R., Kick, G.J., Hyatt, D., Dill, B.D., Land, M.L., Verberkmoes, N.C., Hettich, R.L., and Banfield, J.F., 2010. Enigmatic, ultrasmall, uncultivated archaea. Proceedings of the National Academy of Sciences USA. vol. 107. no. 19, pp. 8806–8811.

Nordstrom, D.K., and Alpers, C.N., 1999. Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. Proceedings of the National Academy of Sciences USA, vol. 96, pp. 3455–3462.

Nordstrom, D.K., Jenne, E.A., and Averett, R.C., 1977. Heavy Metal Discharges into Shasta Lake and Keswick Reservoir on the Sacramento River, California: A Reconnaissance During Low Flow. Open-File Report 76-49. U.S. Geological Survey, Reston, VA.

Nordstrom, D.K., Alpers, C.N., Coston, J.A., Taylor, H.E., McCleskey, R.B., Ball, J.W., Ogle, S., Cotsifas, J.S., and Davis, J.A., 1999. Geochemistry, Toxicity, and Sorption Properties of Contaminated Sediments and Pore Waters from Two Reservoirs Receiving Mine Drainage. Water-Resources Investigation Report 99-4018A, U.S. Geological Survey, Reston, VA, pp. 289-296.

Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., and Blowes, D.W., 2000. Negative pH and extremely acidic mine waters from Iron Mountain, California. Environmental Science and Technology, vol. 34, no. 2, pp. 254–258.

Robbins, E.I., Rodgers, T.M., Alpers, C.N., and Nordstrom, D.K., 2000. Ecogeochemistry of the subsurface food web at pH 0–2.5 in Iron Mountain, California, USA. Hydrobiologia, vol. 433, pp. 15–23.

U.S. Environmental Protection Agency, 2000. Proposed $862 Million Settlement to Pay for Iron Mountain Mine Cleanup. Iron Mountain Mine Superfund site memo. EPA Region 9, 2 pp.

U.S. Environmental Protection Agency, 2006. Abandoned Mine Lands Case Study: Iron Mountain Mine, March 07, 2006, 17 pp. http://www.epa.gov/aml/tech/imm.pdf. Retrived December 19, 2013.

U.S. Environmental Protection Agency, 2009. Iron Mountain Mine Superfund site: EPA Accelerating Cleanup Efforts at Iron Mountain Mine Site Supporting Local Economy with Recovery Act Funds. EPA, Region 9. U.S. EPA, Washington, DC.

U.S. Environmental Protection Agency, 2010. Site Status Report, Iron Mountain Mine, EPA Superfund Program. EPA CAD980498612. EPA Region 9. http://yosemite.epa.gov/R9/SFUND/R9SFDOCW.NSF/VIEWBYEPAID/CAD980498612?OPENDOCUMENT#descr, 3 pp.

32
OVERVIEW OF RESOURCES FROM ACID DRAINAGE AND POSTMINING OPPORTUNITIES

JAMES A. JACOBS

It is estimated, but not accurately known, that well over 100,000 abandoned mine lands (AMLs) across the United States (U.S. Environmental Protection Agency, 2012), and these types of abandoned sites are found all too commonly throughout the world. In the past, once the valuable ores were removed from a mine site, the miners moved on to the next claim, without environmental site restoration. Abandoned mine lands, many with acid mine drainage; create new environmental challenges as well as potential sustainable, long-term business opportunities for local communities. This chapter focuses on concepts of sustainable restoration and reuse of mine sites and postmining opportunities in resource recovery, education and training, local employment, science research, energy production, ecosystem services, tourism, and other potential areas.

Green and Sustainable Remediation of Acid Mine Drainage Sites

In an effort to provide reasonable reclamation options that take into account pollution caused by mine restoration activities, the community needs and other issues for industrial and mining properties, the U.S. Environmental Protection Agency (EPA) and others have developed sustainable remediation goals. Green and sustainable remediation considers the environmental impacts of site restoration projects and implements measures to mitigate these environmental impacts and to increase the overall sustainability of mine site remedies (Figure 32.1). The main concept of green remediation is to obtain optimal sustainable revitalization in a project by striving for balance between environmental, economic, and social aspects (California Environmental Protection Agency, 2009). Over the past decade, green remediation and sustainable practices have become popular not only in the United States and Canada, but in Europe and Asia as well. The U.S. EPA and other regulatory organizations have developed green and sustainable remediation procedures and guidelines. State regulatory agencies, such as the California Department of Toxic Substances Control (California Environmental Protection Agency, 2009) have published protocols and guidelines for green remediation. The Interstate Technology and Regulatory Council developed two publications on green and sustainable remediation (ITRC, 2011a,b). The Network for Industrially Contaminated Land in Europe (NICOLE) is providing sustainable remediation leadership on the continent. Another organization is the Sustainable Remediation Forum (SURF), which focuses on developing white papers (Ellis and Hadley, 2009) and policies. ASTM International, formerly known as the American Society for Testing and Materials (ASTM), has convened the ASTM Greener Cleanup Standard Practice group to develop standard practices in sustainable remediation. ASTM International has also prepared the Standard Guide for Integrating Sustainable Objectives into Cleanup. The core elements of sustainability for the U.S. government, which were developed by the U.S. EPA in accordance with Executive Order 13423 and are outlined in the green remediation EPA Technology Primer, are (1) air; (2) water; (3) land and ecosystems; (4) materials and waste; (5) energy; and (6) stewardship. These approaches should be used for planning and implementing restoration and remediation at former mine sites.

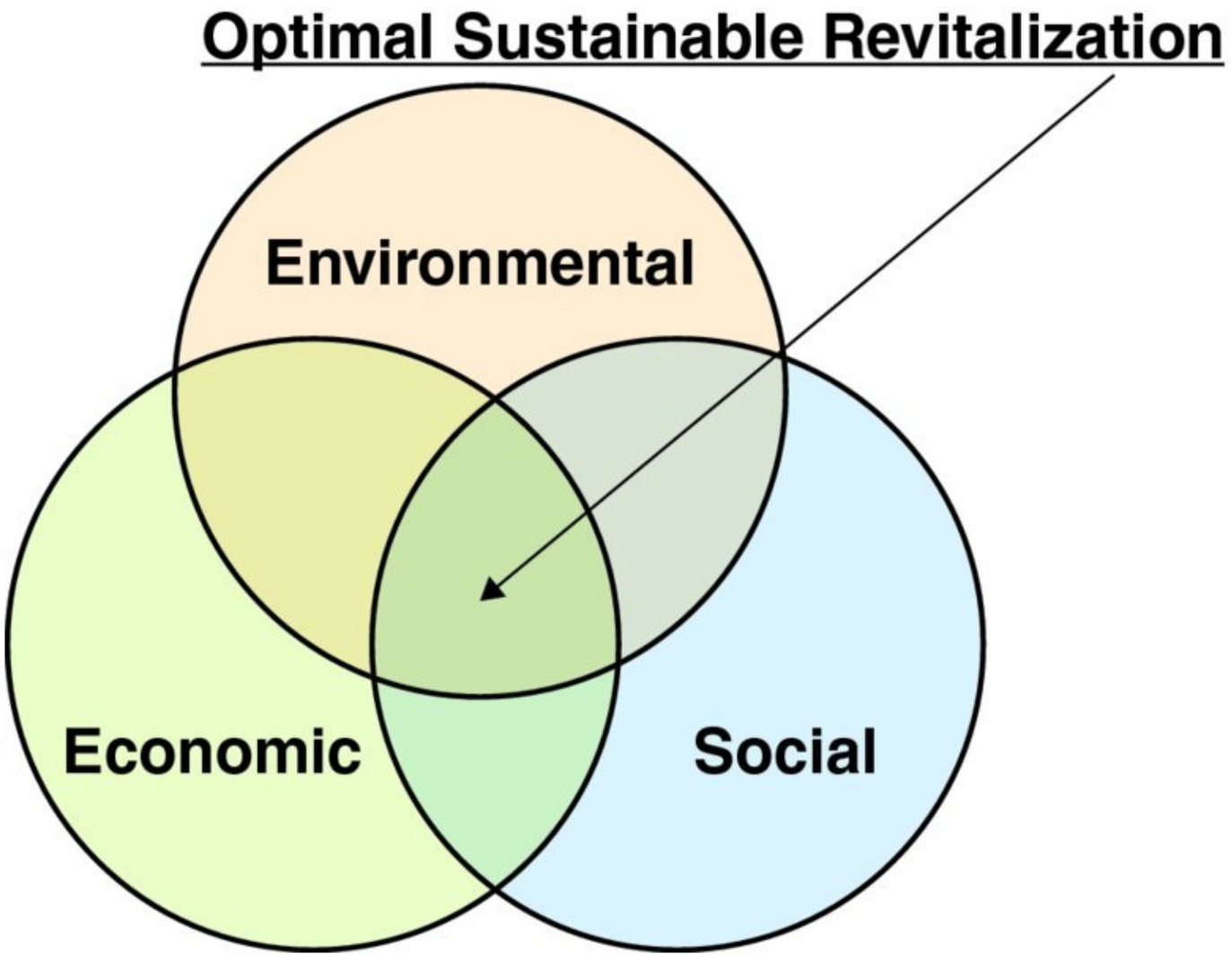

FIGURE 32.1 Concept of sustainable remediation. (From the California Environmental Protection Agency, 2009.)

The regulatory drive to develop a more sustainable approach to assessment and site restoration at mine sites and industrial properties was developed from the realization that all of contamination in the environment is not only impossible but also undesirable to remove completely, and that as long as the impact on sensitive receptors have been minimized and are below regulatory-approved levels, other factors should be considered in the goal of case closure. Other case closure factors to be taken into account include energy use, air and atmospheric pollution generated during cleanup activities, water resources affected or consumed during the remediation project, land and ecosystem resources and use that might be affected by the cleanup, and materials and waste generation during remedial tasks (Figure 32.2). Excavating soil from an oil spill and moving it to a landfill generates greenhouse gases (carbon dioxide) as part of the vehicle use, consumes energy (diesel fuel), contributes to traffic and community congestion on the streets, and so on (Figures 32.3 and 32.4). These activities also contribute to local employment and economic gains for the community. The California Environmental Protection Agency's Green Remediation Evaluation Matrix is a qualitative approach toward obtaining the goals of sustainable and green remediation by identifying key areas for improvement or opportunities for reducing impacts on remedial options. Table 32.1 provides the stressors and affected media for specific types of remedial activities as described by the California Environmental Protection Agency (2009).

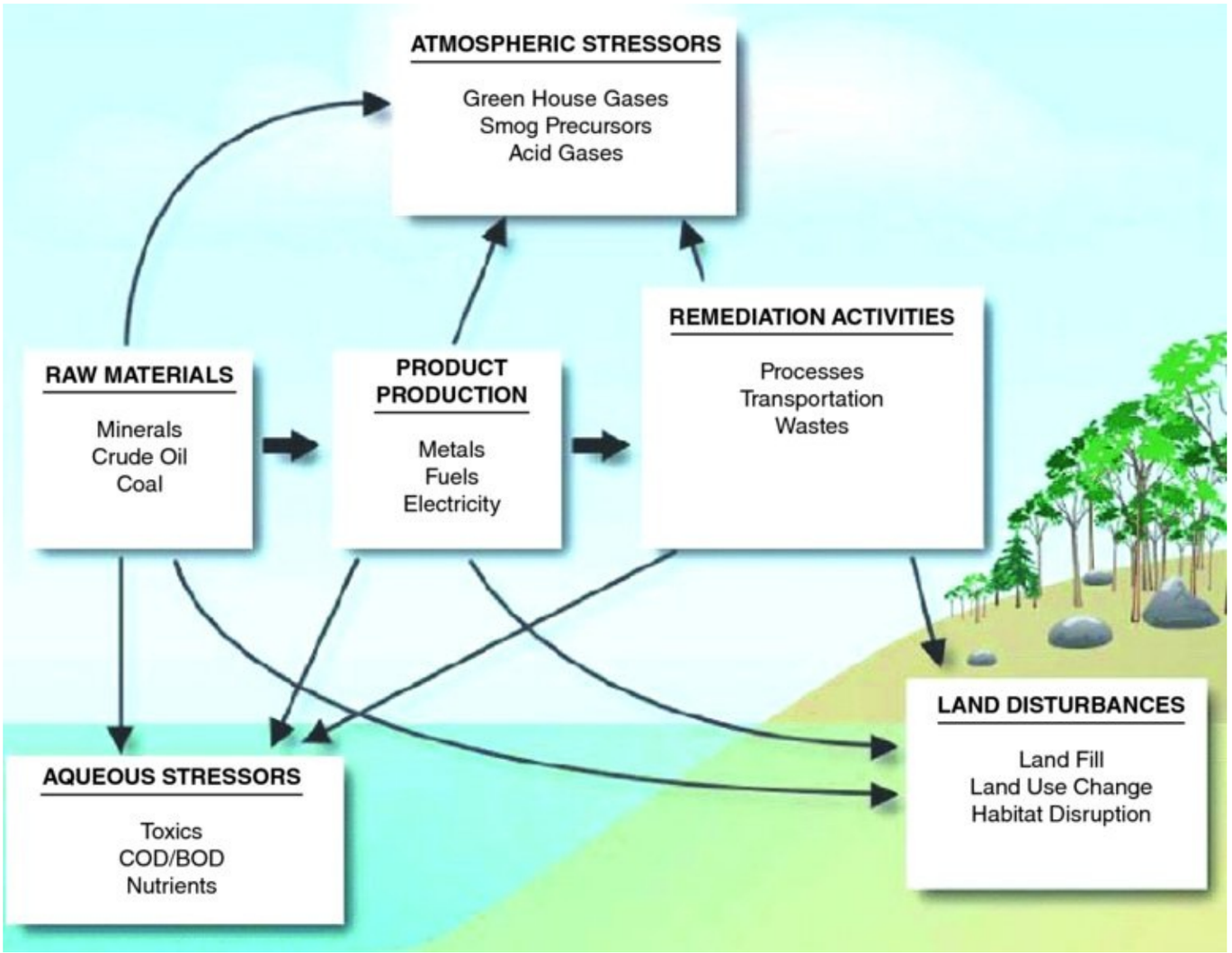

FIGURE 32.2 Life-cycle diagram for sustainable remediation. (From the California Environmental Protection Agency, 2009.)

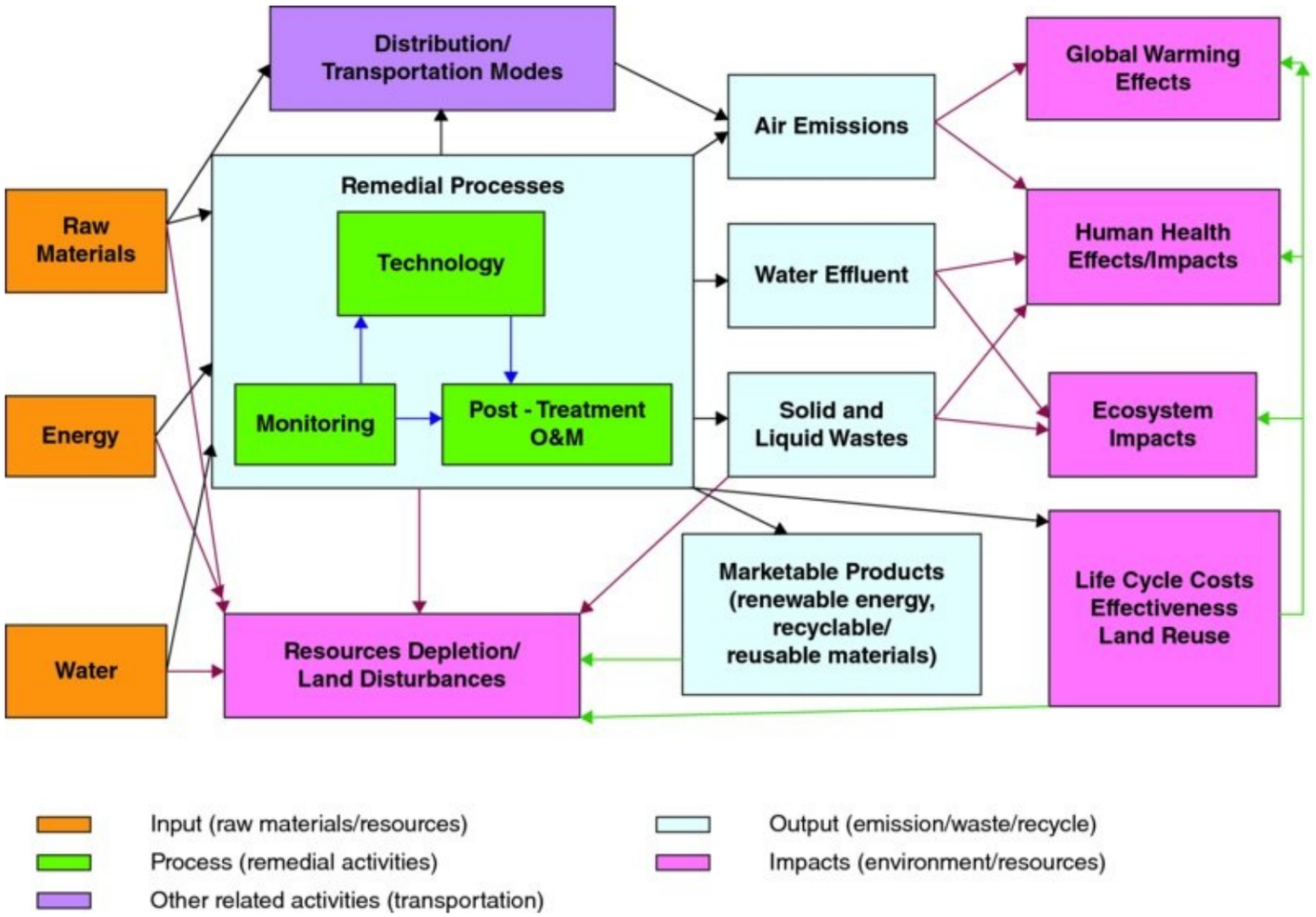

FIGURE 32.3 Life-cycle evaluation framework diagram. (From the California Environmental Protection Agency, 2009.)

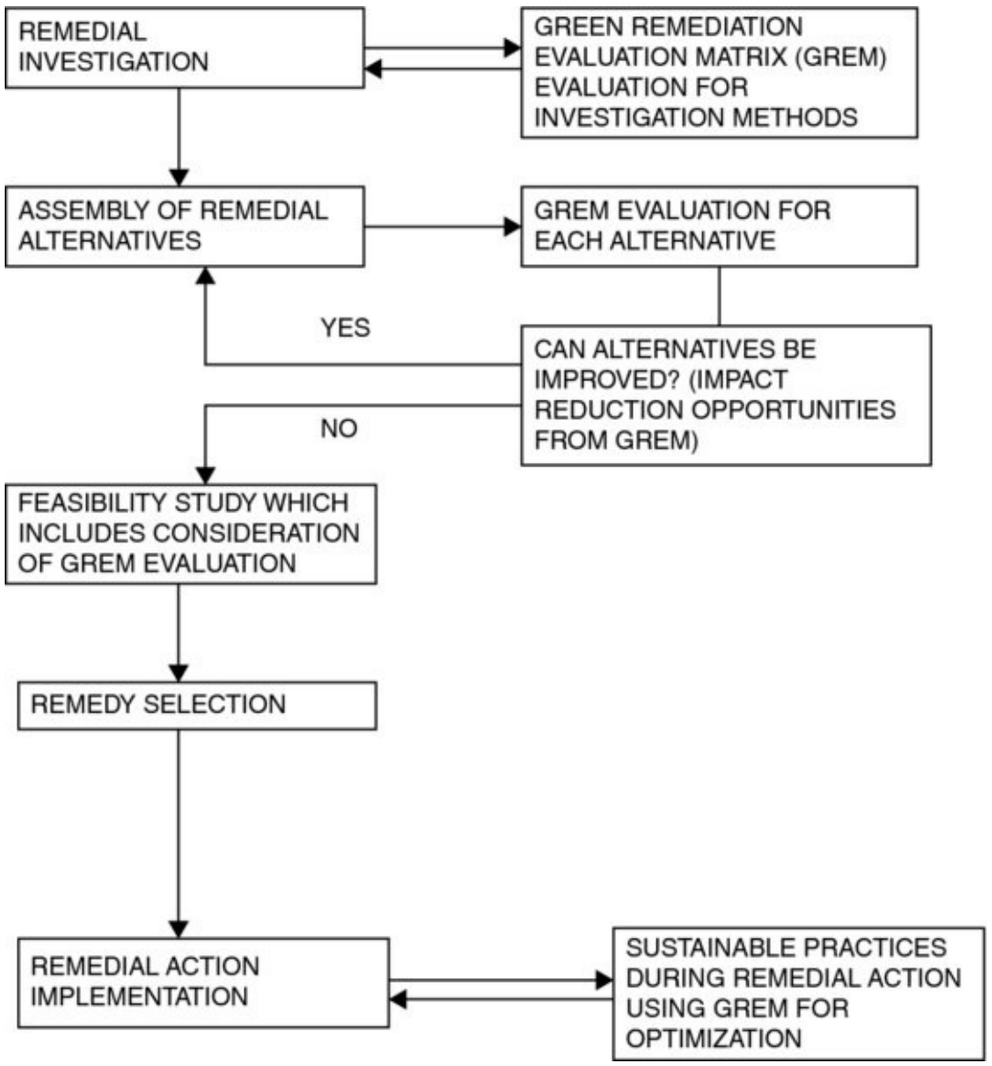

FIGURE 32.4 Green remediation evaluation matrix flowchart. (From the California Environmental Protection Agency, 2009.)

TABLE 32.1 Green Remediation Evaluation Matrix[a]

Stressors	Affected Media	Mechanism/Effect	Y/N[b]	Score
Substance release/production				
Airborne NO_x and SO_x	Air	Acid rain and photochemical smog		
Chlorofluorocarbon vapors	Air	Ozone depletion		
Greenhouse gas emissions	Air	Atmospheric warming		
Airborne particulates/toxic vapors/gases/water vapor	Air	General air pollution/toxic air/humidity increase		
Liquid waste production	Water	Water toxicity/sediment toxicity/sediment		
Solid waste production	Land	Land use/toxicity		
Thermal releases				
Warm water	Water	Habitat warming		
Warm vapor	Air	Atmospheric humidity		
Physical disturbances/disruptions				
Soil structure disruption	Land	Habitat destruction/soil infertility		
Noise/odor/vibration/aesthetics	General environment	Nuisance and safety		
Traffic	Land; general environment	Nuisance and safety		
Land stagnation	Land; general environment	Remediation time; cleanup efficiency; re-development		
Resource depletion/gain (recycling)				
Petroleum (energy)	Subsurface	Consumption		
Mineral	Subsurface	Consumption		
Construction materials (soil/concrete/plastic)	Land	Consumption/reuse		
Land and space	Land	Impoundment/reuse		
Surface water and groundwater	Water, land (subsidence)	Impoundment/sequester/ reuse		
Biology resources (plants/trees/animals/microorganisms)	Air, water, land/forest, subsurface	Species disappearance/diversity reduction/regenerative ability reduction		

Source: California Environmental Protection Agency (2009).

[a]Use for evaluating one technology or remedial alternative as a checklist. Expand for alternative comparison by adding additional score columns for each alternative.

[b]State whether the impact applies or does not apply to the alternative and continue the evaluation.

Green and sustainable remediation best management practices (BMPs) are design elements that mitigate the potential negative environmental impacts of site investigation and remedy implementation activities and increase the overall sustainability of the cleanup project. The BMPs achieve the green and sustainable remediation goals by:

- Reducing the quantity of energy and nonrenewable resources required to implement site remedies
- Reducing the quantity of emissions and waste generated as remedy by-products
- Improving community relations (and realizing other social benefits) during the site cleanup process

A series of computer models evaluating different sustainability issues and cost options of soil and groundwater remediation have been developed. Although designed originally for industrial contamination, the green and sustainable concepts and computer models can easily be applied and adapted to mine land restoration. One free and publically available sustainable remediation evaluation tool was created by the U.S. Navy and co-developed by Battelle. The model, called SiteWise, is a stand-alone tool that assesses the environmental footprint of remedial actions addressing cost, remediation effectiveness, and protection of human health and the environment using the following sustainability metrics:

Metrics calculated with the SiteWise tool:

- Energy consumption (expressed as Btu)
- GHG emissions (metric tons of CO^{2-}, CH_4, N_2O)
- Criteria pollutant emissions (metric tons of NO_x, So_x, PM)
- Water impacts (water consumption in gallons)
- Worker safety (accidental injury and death)

Metrics evaluated outside the SiteWise tool:

- Ecological impacts
- Resource Consumption (land, topsoil, surface water and aquifer impacts, landfill space)
- Community Impacts (noise, traffic, odors, etc.)

Environmental Footprint Assessment Methodology

An environmental footprint can be assessed to determine which potential remedies and which elements of the remedy have the greatest environmental footprint. This allows the remediation project manager to better focus on footprint reduction methods. The evaluation should include effects from on- and off-site actions and consider alternative energy sources and more energy-efficient alternatives for high-energy demand remedies. A more comprehensive evaluation could also consider impacts from raw materials, supplies, and manufacturing of equipment required for remedial actions. The remediation industry has not yet developed standard methods of performing these assessments; however, information that can be used to perform an analysis is available from several recognizable sources. Several examples of sources are presented below.

Footprint Reduction Methods

Methods of reducing the environmental footprint are also presented in U.S. EPA publications, such as *Incorporating Sustainable Environmental Practices into Remediation of Contamination Sites* U.S.

Environmental Protection Agency, 2008b) and *Green Remediation: Best Management Practices for Excavation and Surface Restoration* (U.S. Environmental Protection Agency, 2008c) and may also include provisions related to landscape alteration, where the concepts and resources are similar in scope to the "Sustainable Sites" section of the "Leadership in Energy and Environment Design (LEED) for Core and Shell" development framework found in LEED.

Sustainable Remediation Tool

Another free and publically available sustainable remediation tool, originally designed for industrial contamination, was created by the Air Force Center for Environmental Excellence and its partners. The sustainable remediation tool (SRT), like other computer tools, includes concepts that can easily be adapted for mine restoration activities. The SRT serves two general purposes: (1) in planning for future implementation of remediation technologies at a particular mine site, and (2) as a means to evaluate optimization of remediation technology systems already in place or to compare remediation approaches based on sustainability metrics.

Technologies potentially applicable to mine restoration evaluated with the site remediation tool include:

- Excavation (soil and mining wastes)
- Pump and treat (groundwater)
- Enhanced in situ biodegradation (primarily ground- water)
- Enhanced ex situ biodegradation (modified SRT; primarily surface water)
- Permeable reactive barrier (groundwater and modified SRT for surface water)
- Long-term monitoring/monitored natural attenuation (groundwater and modified SRT for surface water)

Metrics calculated with the site remediation tool include:

- Carbon dioxide emissions
- Nitrogen oxide emissions
- Sulfur oxide emissions
- PM_{10}
- Total energy consumed
- Change in resource service
- Technology cost
- Safety and accident risk

The site remediation tool is structured into risk-based corrective action tool kit-type tiers. Privately available green and sustainable computer models with more options are also available.

Postmining Opportunities

Postmining planning and restoration eventually occur in the life cycle of all mining operations, whether or not they have acid mine drainage. Due to the large number of orphan, abandoned, disused, or unprofitable

mine sites worldwide, less conventional and unusual partnerships are needed to restore the environment after mining and create sustainable community opportunities. Postmining opportunities have been developed in many countries over the past decade. The Eden Project near St. Blazey in Cornwall, UK, is a former kaolinite open-pit mine used to make china that was reinvented as one of the world's largest greenhouse, containing artificial biomes. The plants showcased in the giant domed structures have been collected from around the world. The steel-framed domed structures consist of hundreds of hexagonal and pentagonal inflated plastic cells. The domed structures feature a tropical and Mediterranean plant ecosystem (Pearman, 2009).

Success in the postmining era requires not only government legislation to set environmental restoration standards, but also significant input from the community and likely third-party grants and funding. The socioeconomic issues to address are not just the loss of important mining jobs and the self-esteem of former workers but also the new identity of the postmining community. It is not surprising that many postmining areas have an overabundance of unemployed workers. Postmining restoration activities sponsored with government grants can include job training of environmental and engineering certificate or university classes which provide college credit for internships combined with workshops and environmental restoration training. Aquaculture and locally grown food can be part of the grand restoration concept as well as developing ecosystem services associated with developing a sustainable wildlife and tourist economy should historical and ecological resources be available. According to the Eden Project (Pearman, 2009), successful projects used local solutions to fit the details of the local circumstances. Local leadership with a commitment and vision from the community is required for sustainable mine site regeneration. Working with shared interests, creative partnerships for grants, funding, and development can place unusual partners together in the mix for a sustainable postmining opportunity. In some historic mining areas with a nondiversified economy, a postmining redevelopment should include hybrid projects and multipurpose sites to provide the diversity in the local area. For postmining sites that provide entertainment, tourism, or other visitor-dependent opportunities, established transportation links with easy connections and the ability to link hotels and restaurants easily with other visitor attractions allow for a more successful outcome.

Although not all mine sites that have been redeveloped successfully are associated with acid mine drainage, many are, and creative redevelopment concepts and community-repositioning ideas are presented by Pearman (2009). A selected list of potential reuses of mine sites includes community redevelopment to provide new opportunities in the following categories:

- Energy generation
- Entertainment and tourism
- Ecosystem and habitat restoration
- Food production and water recycling
- Human health and therapy
- Mining heritage and tourism
- Infrastructure services
- Re-mining and resource recovery
- Science and technology
- Sport

Energy Generation

For the energy category, former mine sites have been used in a variety of sustainable energy production projects. Most projects had a significant level of assistance from government or nongovernment organizations in the form of grants, matching funding, or tax incentives. Energy projects which can be part of the erosion control plantings include harvesting biofuels in areas unsuitable for growing food crops, such as the Dinslaken site at Emscher Park in the coal-rich Ruhr area of Germany. Up to 10,000 ha of former coal-mined land will be used to grow fast-growing willow and poplar trees that will provide biomass for local heat generation. Coal mines have long been associated with coal bed methane (CBM). In historical coal areas where deposits are rich in methane gas, power plants are capturing and using the CBM before it escapes from the abandoned mines and seeps into the atmosphere as a greenhouse gas. An example of a CBM site used for energy production is the Hickelton power plant in South Yorkshire, UK. Two pump-storage hydroelectric power stations were developed in the former open-pit mines at Dinorwig in Snowdonia, Wales and at Misima Island in Papua New Guinea. The pump-storage concept uses a system of pumps and lakes or pits to store water. The water is pumped to the high points, such as lakes or pits, when electricity is inexpensive, and the water can be released by gravity to generate power when additional electricity is needed in the area. With a concept similar to that of hydroelectric pump-storage dams, compressed air energy storage (CAES) systems store excess energy from coal-fired power stations during off-peak periods by storing it as pressurized air in mine shafts, as potential energy. CAES systems inject compressed air into the subsurface mine, and when electricity is needed at peak periods, the compressed air is withdrawn and used with fuel to operate power-generating air turbines. A site in Norton, Ohio is associated with CAES technology.

In windy areas, wind power can be a popular reuse of mine sites as long as government subsidies continue to make them economically viable. Abandoned mine lands may be in areas that are ill-suited for more traditional commercial or industrial reuse opportunities. However, the abandoned mine lands can be good locations for wind farms. Wind farms require large, open sites and a steady and sufficient supply of wind. Abandoned mine lands are frequently associated with large sites in mountainous areas that receive consistent wind flows. The sites are also frequently located near existing infrastructure including highways, roads, and power-transmission lines (U.S. Environmental Protection Agency, 2012). An example is the Somerset Wind Farm in southwestern Pennsylvania in the windy Laurel Highlands along the well-traveled Pennsylvania Turnpike. A former coal mining area, the wind farm (Figures 32.5 and 32.6) was a joint venture of two energy companies. In 2001, six 1.5-MW wind turbines were operational. Currently, the Somerset Wind Farm should produce as much as 1000 MWH enough to supply perhaps 800 homes with electricity.

FIGURE 32.5 Wind turbines at the former coal mine at Somerset Wind Farm. (From U.S. Environmental Protection Agency, 2012.)

FIGURE 32.6 Close-up of the wind turbines at the Somerset Wind Farm. (From U.S. Environmental Protection Agency, 2012.)

Other wind energy projects at former mine sites include the Klettwitz, Brandeberg Wind Farm in Germany and the Black Law Wind Farm in Forth, Scotland. For mines near the ocean, tidal power energy in the WaveShaft concept is being tried in Cornwall, England. Researchers noted that the tidal changes create an airflow through the mine as abandoned mine shafts are flooded and drained. As the airflow moves in and out of the abandoned mine shafts, the air could ultimately generate energy by turning wind turbines. Solar power from photovoltaic systems can be attractive at former mine sites having low-cost land that are located near energy customers. An example of a solar photovoltaic system at a former mine site is the Geosol site in Espenhain, Germany. A flooded coal mine beneath city streets in Glasgow, Scotland was used to create a geothermal heating system for residents. About 328 ft (about 100 m) beneath the ground surface, water in the former mine is at a steady 54°F (12°C), making possible the use of heat pumps for residential geothermal energy. A site in the Dutch city of Heerlen in Limburg has former coal mines that have flooded abandoned mine shafts where water stays at a constant temperature and is used for residential geothermal systems (Pearman, 2009).

Entertainment and Tourism

Entertainment venues require massive transportation hubs with associated hotels, restaurants, and tourism support services. Nonetheless, there are dozens of examples where successful re-imagining of former

mine sites into new community uses have been documented. A phosphate mine in the town of Langebaanweg area near Cape Town, South Africa has been repositioned as a fossil discovery site, with over 200 different types of animals from about 5 million years ago. The former mine is now associated in a partnership with the Iziko Museums in Cape Town which converted the 700-ha site into a scientific and ecotourism destination. The former mine was listed as a national monument in 1996. A former limestone mine in Dalhalla, Sweden is located in a tourist area and provides an unusual setting for a music and performance venue. The exceptional acoustic qualities of the former open-pit limestone mine created a natural amphitheater and dramatic stage for a 4500-seat opera house. As seen in other success stories, transportation links in this popular Swedish tourist area encouraged the redevelopment of the former open-pit mine. Other open-air theaters have been fashioned out of redesigned coal spoil piles such as the one at Halde Haniel, in Bottrop, Germany. The Ruhr Area National Geopark was built on the historical interest of mining and industrial history in the Ruhr region of Germany. The Geopark features geological and science exhibits for the general public. A 200-ha theme park site with six roller coasters is featured at Thorpe Park in Surrey, England. The well-known Wieliczka salt mine in Poland provides tours and has several chambers of underground rooms for banquets, weddings, and fine dining. The former rock-crushing room at the silver mine at El Edén in Zacatecas, Mexico is now the La Mina Club, a popular nightclub with a high-tech sound system located 1181 ft (360 m) below ground surface. Tourists can explore the silver mine during the day, while at night, the historical mining town uses an underground train to deliver guests to the La Mina Club. The historical silver mine dates back to the late sixteenth century. The Dolcoath mine at Camborne in Cornwall, England is now a performance arts community project where a local theater company entertains the community and tourists. The Ferropolis open-air concert venue in Dessau, Germany includes historical coal-mining equipment and a vast artificial lake to create an outdoor mining museum and performance site. Some former mine sites have environments that are valued by filmmakers; for example, the Bartertown scenes in the *Mad Max* movie were filmed at the Homebush Bay mine in Sydney, Australia.

Ecosystem and Habitat Restoration

Restored mine sites have been used as arboretums, storm water retention areas, natural wetlands, wildlife refuges, bird sanctuaries, community parks, hiking and bicycle trails, and golf courses. Some former open-pit mines have been used as recreational lakes for tourism, such as the china clay pit in Cornwall, UK and the Nussloch quarry in Baden-Wurttemberg, Germany, where ecosystem restoration is enhanced by outdoor activities that can be supported in the former mining areas. Tourist activities include sailing, fishing, horse back riding, hiking, cycling, bird and animal watching, and camping.

The Spenceville mine near Sacramento, California produced copper for about 20 years starting in 1862, until the underground working collapsed. A cooperative approach included the interaction of various local, state, and federal government agencies as well as community environmental groups and residents who worked together to accomplish ecosystem restoration, which included the treatment of the mine wastes and a flooded mine pit which was filled with acid mine drainage having a pH of 2.5 (Figure 32.7). During site restoration of the mine site, cultural and mining-related artifacts were exhumed, surveyed, cataloged, and preserved. The former Spenceville mine site has been fully reclaimed (Reynolds, 2008) and is now part of the larger Spenceville Wildlife Area, which contains 11,213 acres (4537 ha). Since restoration, over 175 species of birds have been identified in the area (Reynolds, 2012). The restored ecosystem at the Spenceville Wildlife Area is easily accessible and is one more draw for outdoor-oriented visitors, who have a choice of many tourist activities in the mother-lode gold country near Grass Valley and Nevada City, California (Figure 32.8). Since tourism has been part of the local economy for over a century, efforts to restore the Spenceville mine as a wildlife preserve complemented the already

significant local tourist business infrastructure. Many other successful mine reuse projects build on the existing local business strengths.

FIGURE 32.7 Spenceville mine in northern California prior to reclamation in about 2000. The pit contained 7.5 million gallons (28.4 L) of pH 2.5 acid mine waters. (Courtesy of the California Geological Survey.)

FIGURE 32.8 Spenceville mine in northern California in 2012 after extensive site reclamation in the same general area as in Figure 32.7. (Courtesy of James A. Jacobs.)

Food Production and Water Recycling

Aquaculture has developed in a variety of coal-mining states, including West Virginia, Maryland, and Pennsylvania, where high-flow mine water is treated and used as a source of water for aquiculture. Rainbow trout, largemouth bass, hybrid striped bass, and hybrid bluegill have all been grown. Aquaculture can be an important part of mine reclamation as well as providing a locally grown food source and a sustainable business. Water reuse is significant as long as dissolved trace metals can be removed and the pH restored to levels optimal for fish (Semmens et al., 2003; Semmens and Miller, 2003). Aquaculture is also part of a state government program with the local coal-mining company at Collie in Western Australia, where freshwater crayfish called marron are being grown and harvested. In addition to food production, the goal was to develop a sustainable aboriginal training program in aquaculture that would also provide business, social, and educational benefits to the local Ngalang Boodja community. The constant temperature [54 to 57°F (12 to 14°C)] and humidity (90%) of former underground mines such as the one in Moldova provide opportunities for wine storage. The 24 miles (39 km) of wine caves at Cricova are used for wine storage; valuable bottles of product are housed in the once-used adits of a limestone mine outside the city of Chisinau in Moldova.

In desert areas or in times of drought, recycling of treated acid mine water for agricultural or other uses could add to limited water resources. Reclaimed mine sites have been restored to farmland throughout the world. Historical surface coal mines in Pennsylvania, Ohio, Indiana, and Illinois have been reclaimed after mining for crop and livestock reuse (Pearman, 2009). In a region that has had wine production for

centuries, Bohemia is well known for spirited beverages. It is also an area with shallow lignite deposits. The former lignite surface mine sites have been reclaimed at Most in the Czech Republic, where vineyards are now part of a planned diversification program of the local economy.

The constant temperature and humidity and dark conditions are optimal for mushroom farming in the tunnels of an underground limestone mine in Worthington, Pennsylvania. Organic vegetables are being processed at the Vryheid Coronation Colliery in South Africa, where a coking coal site is now used for food processing, increasing local employment. A local food cooperative working in an adit of an old copper mine at Valepelline in the Aosta Valley in Italy is used to age Fontina cheese. The cheese storehouse in the Italian Alps uses some of the same transportation infrastructure, such as the ore car tracks that were once used for transporting copper ore.

Human Health and Therapy

Medicinal uses of abandoned mines have been used by thousands of people seeking restorative health effects. The Pyhäsalmi facility is a former copper and zinc mine in central Finland. At a depth of 4724 ft (1440 m), the former mine is now used as a deep underground sauna. The Wieliczka salt mine in Poland is used by patients with respiratory conditions requiring air of exceptional purity with a stable temperature and high relative humidity. Although not a mainstream medical treatment method, some patients suffering from chronic pain use radon therapy at a former gold mine at Bad Gastein facility in the Austrian Alps. A similar radon treatment facility is available at the inactive Merry Widow gold mine near Basin, Montana.

Mining Heritage and Tourism

The products of gold, silver and diamond mines appeal to many visitors, and general interest in the geology of ore deposits and history of mining and tourist activities is indicated by the large number of Mining World Heritage Sites (Table 32.2).

TABLE 32.2 Mining World Heritage Sites

Country	Site
Austria	Hallstatt–Dachstein Salzkammergut cultural landscape
Belgium	Neolithic flint mines at Spiennes
Bolivia	Potosí City
Brazil	Historic town of Ouro Preto
	Historic center of the town of Diamantina
	Historic center of the town of Goiás
Chile	Humberstone and Santa Laura saltpeter works
	Sewell mining town
Czech Republic	Kutná Hora
Germany	Rammelsberg mines and the historic town of Goslar
	Zollverein coal mine industrial complex, Essen
Japan	Iwami Ginzan silver mine
Mexico	Guanajuato town and adjacent silver mines
	Zacatecas silver mines
Norway	Røros mining town
Poland	Wieliczka salt mine
Slovakia	Banská Štiavnica medieval mining center
Spain	Las Médulas
Sweden	Great Copper Mountain, Falun
UK	Cornwall and West Devon mining landscape, Cornwall
	Ironbridge Gorge
	Blaenavon Industrial Landscape

Source: Pearman (2009).

For those visitors wanting an underground mining experience, the Fokis mine at Vagonetto, Greece provides tours of the historical underground bauxite mine. Another site in Greece is the ancient surface mining area of Dionyssos, where the marble used to build the Parthenon was quarried. Marble waste rock piles dating back to the fifth century B.S. exist at the quarry site. A guided tour is available of the underground workings of the Geevor tin mine in Cornwall, UK. An open-pit copper mine with potential lead, silver, zinc, and gold deposits is a tourist attraction at Parys Mountain in Anglesey in northern Wales. The Las Médulas gold mine in northwestern Spain is a World Heritage Site, being an important gold mining area for the Roman Empire. The ancient Roman mining technology is visible, as systems of aqueducts were used for hydraulic power in the mine operations. Mining waste piles from the Roman era are still visible today. The silver mines of the UNESCO-protected town of Kutná Hora in the Czech Republic were first worked in the thirteenth century. A royal mint was established there, and the mine sites and city bring in tourists interested in the rich mining history of the region. For those interested in mining technology, the Mining Hall of Fame in Kalgoorlie, Australia features the above- and underground gold mining history of the region. The Big Pit at Blaenavon in southern Wales is a mining museum at the

Blaenavon World Heritage Site in a former coal mine. Exhibits and collections of the coal mines and buildings feature historical and scientific exhibits to attract visitors to the region.

The Big Hole at Kimberly in South Africa is the site of the origin of the modern diamond industry. The pit itself features a cantilevered viewing platform, and an underground experience is offered as well. Many of the original buildings from the mining town are part of the historical appeal. The entire well-preserved mining city of Potsí in Bolivia features a high-altitude silver mining area that has existed for hundreds of years. Potsí became a World Heritage Site in 1987. Another World Heritage Site, the abandoned copper-mining town of Sewell in Cachapoal in Chile is located at 6562 ft (2000 m). The town was built to support workers at the large El Teniente underground copper mine. The city is served only by a railway station and is built on the side of a mountain, providing glimpses into historical metal-mining practices in South America.

A variety of mining sites are open for historical tours in the United States. An example is the Mollie Kathleen gold mine in Cripple Creek, Colorado, where tourists can safely descend 1000 ft (305 m) into the underground workings and briefly experience the challenges to gold miners. Another example of a historical mine open to the public is the Sutter gold mine in Sutter Creek, California, where the tour focuses on educating visitors about life inside a gold mine, the safety issues involved, and the geology of ore deposits. The lure of gold mining in rustic settings with reasonable transportation connections can create tourist attractions at former mine sites.

Infrastructure Services

A data storage facility is located in a formerly active salt mine at Hutchinson, Kansas. Due to the constant temperature, humidity, dryness, and gas-free atmosphere, the facility provides private and secure vaults used by a variety of different industries for long-term data storage. The Winsford salt mine at Cheshire in the UK is also used for fragile and sensitive document storage. There is an electronic data center in Japan, located in an abandoned coal mine in Chubu, Honshu. Due to the need for constant and cool temperatures for computer servers, groundwater is used as a coolant to provide lower energy costs for the center. A desalination plant with a reverse-osmosis water treatment system has been built at Witbank, South Africa. Although the water treatment plant was originally built for the affected waters from the underground coal mine, potable supplies of water are now being supplied to local users by the desalination plant. Future water treatment services for the remaining mines in the area are being considered.

Recycling of car batteries is being performed at a battery-recycling plant built in a former lead, copper, and silver mine at Braubach, Germany. Open-pit mines are being used for landfills when groundwater is below the pit base. Landfills in former open-pit mines can use anaerobic bioreactor designs to increase and optimize biological degradation rates of organic wastes to maximize methane production. In these cases, the methane produced can be captured to produce green electricity, as in the case of the Woodlawn bioreactor landfill in New South Wales in Australia. A former open-pit gold and silver mine near Cajamarca was retrofitted with an impermeable liner to protect and store treated rainwater for the dry season in the San Jose reservoir in Yanachocha, Peru.

In the dry western United States, new water reservoirs formed by damming rivers is unlikely, due to ecological damage to fish species based on the past century of reservoir construction. However, impermeable spray-on liners and specialized geotextile fabrics can convert a former open-pit mine into a water treatment facility for local water storage. The hilly area of Pikeville in eastern Kentucky is part of the Appalachian Mountains, with a long history of bituminous coal mining. Using the controversial and ecologically destructive mountaintop removal as a primary coal mining method in the area resulted in numerous well-drained flattened former mining areas. One such area provided space for the local airport

in Pikeville. Mountaintop removal other mining locations in eastern Kentucky resulted in land that was later redeveloped for shopping malls, prisons, farming, industry, schools, hospitals, and other uses. A large shopping center at Bluewater at Greenhithe in Kent in the UK was built in a former chalk quarry. Redesign of the quarry space provided new economic opportunities for the local community.

Re-mining and Resource Recovery

Many of the metals recovery technologies, including the largest industrial stirred tanks and heap recovery systems, utilize bioprocessing methods, many of which have been summarized by Rawlings and Johnson (2007). As metal prices have increased over the past several decades, mining waste piles are being reprocessed using better technologies than the original mining methods, to extract additional resources. Examples include many locations in the gold-rich California Sierra Nevada mountain range, as well as in South Africa and Australia.

Bioleaching

For acid drainage, bioleaching uses iron- and sulfide-oxidizing bacteria to solubilize pyrite and other metals and to extract specific metal resources from their ores. The precipitates from the acid drainage might include iron, aluminum, copper, lead, zinc, arsenic, nickel, molybdenum, gold, silver, cobalt, and other metals. Some advantages associated with bioleaching are that the acid drainage processes in metal-rich sulfur ore mining areas are probably already ongoing. Bioleaching can generally be economical under the right conditions, and some companies have developed processes for metals extraction. Bioleaching, a type of biomining, tends to be a slow process, but it does work for resource recovery.

Bioleaching is biotechnology that involves optimizing the microbial ecosystem in mining rock waste piles that might be hundreds of years old, so that the metal-solubilizing chemical and biological reactions that would otherwise occur slowly and naturally are sped up by enhanced conditions designed for higher reaction rates catalyzed by the microbial communities in water. Commercial-scale bioleaching processes use the same naturally occurring reactions but accelerate the reactions by optimizing conditions: by controlling and enhancing the most favorable microbial species and population, air temperature, water content, moisture content, oxygen content, acidity, buffering capacity, macronutrients, and other factors. Bioleaching has been used for iron, gold, silver, copper, cobalt, nickel, zinc, and uranium.

In the bioleaching process, the valuable residual metals, such as insoluble iron sulfides (pyrite) and other insoluble but valuable metal sulfides, are removed from the waste rocks. The pyrite and associated valuable metals are dissolved in water through microbial catalyzed oxidation and are converted into water-soluble metal sulfates which contain valuable metals, such as gold, silver, copper, and other metals. The resulting liquid metal sulfates such as copper sulfate are recovered by chemical processes such as changing pH or redox conditions or though electrolytic processes. More valuable metals, such as gold and silver, which are generally inert and have low reactivity, are recovered by adding lime to raise the pH and create a metal sludge, which is then processed. Bioleaching requires significant planning and understanding of microbial processes, a modest capital investment, and allows the recovery of metals from low-grade ores and waste rocks. The process is slow compared to removal of the ores from the subsurface in pit or underground mines combined with pyrometallurgical methods such as smelting of extracting the metals. Other advantages to bioleaching include low-temperature reactions and minimal energy requirements. Concerns relate to the control of any contaminants generated, the ability to protect nearby surface water and aquifer supplies, and the available large space required for the process. Bioleaching is a slow process and requires patience for the 6 to 60 months required for enhanced microbial processes to take place. The goal of a bioleaching system is the development of a consistent,

economical, repeatable, and uniformly processed microbial-enhanced metals extraction system which uses waste mining rocks as the source of raw materials.

Acid Recovery

Sulfuric acid was known to the Romans; in antiquity it was known by its historical name, oil of vitriol. Pure sulfuric acid is a highly corrosive, colorless, and viscous liquid. Sulfuric acid is soluble in water at all concentrations. As the most heavily produced chemical in the world, sulfuric acid has many applications: in oil refining, ore processing, fertilizer manufacturing, wastewater treatment, pharmaceutical production, and chemical manufacturing. Sulfuric acid is used in lead–acid batteries as well. As part of bioleaching and metals recovery, although considered a waste product, if prices of bulk sulfuric acid increase greatly, improved industrial processes to refine high-concentration acid drainage for the production of industrial-quality sulfuric acid could occur.

Paint and Dye Recovery

In nature, the neutralization of acid rock drainage, either in situ or at some distance from the source of acid generation, results in a different rock or sediment appearance. In these cases, the rocks, sediments, or soils appear to be oxidized and are different in texture and color from the host source material. Although acid drainage has usually been associated with negative environmental impacts, certain oxidized rock, called *gossans*, are associated with red-brown to yellow-ochre soils. When mixed with water, these colorful oxidized soils have provided early artists with water-soluble paints and dyes. Mineral exploration geologists have used field observations of these colorful soils from natural acid drainage as an aid in mineral exploration (Downing and Mills, 2000). The oxidized rock and sediment chemistry are indicative of potential mineral deposits. Gossans have been a target of mineral prospectors and are easily identified in the field. There are many examples of locating gossans that led to the discovery of major ore bodies and to important economical mining operations.

Pigment Recovery

As part of an environmental restoration project, iron oxide sludge was recovered from a channel at an abandoned coal mine, processed, and used as a raw material in pigment production from a former coal mining and processing facility in southwestern Pennsylvania. Over six decades, a channel carrying mine discharge, estimated to be about 1500 gal/min (5678 L/min) to 1800 gal/min (6814 L/min); pH 6.3, Fe 73 mg/L, alkalinity 313 mg/L as $CaCO_3$, had filled with iron sludge. Approximately 2000 tons of iron sludge was removed and processed for pigments. The sludge was screened and dewatered using frame filter presses. Screening removed vegetative debris, litter, and coal refuse. Dewatering increased the solids content of the product from 25–30% (in place sludge) to 50–52%. A total of 1000 tons of pigment product was trucked to a pigment manufacturer, where it was further dried and calcined, which is a thermal treatment process used for ores. Later the material is milled. The finished product is used to produce pigments from yellow to orange to brown, used in a variety of coloring applications, including paint pigments and clothing dyes. The mine drainage product is replacing mined sources of iron oxide obtained in the United States and imported from Mediterranean and Asian countries (Fish et al., 1996, Hedin, 1998, 2002; Kairies et al., 2001). A selective recycling process was developed for the selective precipitation of iron hydroxide compounds to recover the iron present in acid mine drainage to obtain pigments. The pigments produced were goethite, which was processed into a yellow pigment, and hematite, which was processed into a red pigment. The pigments from this Brazilian study were recommended for paints and colored concretes (Silva et al., 2011).

Science and Technology

Former mine sites have been used in testing science and technology concepts. A former coal mine in Asfordby at Meton Mowbray in Leicestershire in the UK is used to test trains. In the Tytyri mine in Lohja, Finland, an elevator test facility takes advantage of the extremely stable solid rock in the former limestone mine. The elevator test facility extends 1093 ft (333 m) vertically in an unused shaft, where lift speeds of up to 55.7 ft/s (17 m/s) can be tested (Pearman, 2009). The Homestake mine in South Dakota is one of the deepest mines in North America and is used as a science and engineering laboratory. The former gold mine is now used to address research areas in science, including microbiology, biochemistry, particle and nuclear physics, geology, hydrology, and geoengineering. The Parys Mountain facility at Anglesey in northern Wales is used as an ecological laboratory. The mine wastes from the former copper mine site have been used to develop metal-tolerant plant species for various phytoremediation methods. Scientific research was started at the site in the 1950s and focused on plants that could adapt to high concentrations of metals in the mining wastes (Pearman, 2009).

Due to the constant humidity and temperatures underground, some former mine sites have been used as tree nurseries to germinate seedlings for mine reclamation and reforestation. Examples include the underground workings of the Creighton mine in Sudbury, Ontario, Canada, where red pines and jack pines are grown throughout the year for surface planting. Another site is the former lead, zinc, and silver mine at the Bunker Hill Superfund Site in Kellogg, Idaho, where conifer seedlings have been grown since the 1970s in the service tunnels. Carbon sequestration through large-scale reforestation programs at former mine lands can simultaneously sequester large quantities of carbon dioxide while providing erosion control and ecosystem restoration.

Abandoned mine sites are frequently deficient in organic material. Burying organic wastes and composts in mats in former mine sites is a way to sequester carbon and enrich soils for potential agricultural opportunities. Former mine sites in Florida are being used to create organic mats of organic debris left over from the devasting hurricanes. For carbon sequestration, carbon dioxide from nearby coal-fired power plants can be reinjected into abandoned coal mines into the void spaces, adsorbed onto the remaining coal, or dissolved in mine water (Jalili et al., 2011). More research is being performed on carbon sequestration in abandoned coal mines, especially on the significant challenges of sealing of mine shafts and geologic faults, and maintaining carbon dioxide under pressure without creating surface leakage. Subsurface particle physics laboratories have been developed at former mine sites. Examples include the Soudan laboratory in Minnesota, the Super-Kaiokande laboratory in Japan, and the Sudbury Neutrino Observatory in Canada.

Sport

The bare landscape of former mine sites can provide the setting for sports activities. A diving center was developed at the Tidenham Quarry in Chepstow, England as well as the Tauchgasometer in Landschaftspark, Duisburg-Nord in Germany. After decades of silver mining in the area, a ski resort at Park City, Utah has become a world-class ski resort. The Winter Olympics in 2002 was hosted in Park City. An indoor ski slope with a length of 2099 ft (640 m) has been built on the Prosperstraße coal slag pile at the Alpincenter at Bottrop in the Ruhr region of Germany.

Many golf courses have been developed at former mine sites, including the Pete Dye Golf Club in Bridgeport, West Virginia. Built on a former coal mine, the property retains historical coal mine features, including coal mine railroad cars and railroad ties, as well as a former mine shaft that is part of the golf course. An underground cycling track was developed at Sondershausen in Germany in a former salt mine.

A low-oxygen former iron-ore mine provides a hypoxic running track for elite athletes in Yanahara, Japan who wish to train in an environment with less oxygen. The Estádio Municipal de Braga soccer stadium in Braga, Portugal provides unusual seating for 30,000 fans. The stadium, overlooking the city, was built in 2003 in a former quarry carved out of the Monte Cristo granite. Developed in a former limestone quarry in Sweden, the Goland Ring in the Storugns quarry provides an environmentally friendly vehicle-testing facility and motor racing track. The Zollverein Colliery in Essen, Germany features a swimming pool within the coking plant in a historically interesting setting in the city. Also at the Zollverein Colliery is the 492-ft (150-m)-long ice skating rink adjacent to the historical coking ovens in the former coal-producing region of Germany. A former mining area with a need for new industries, Most in the Czech Republic has redeveloped former lignite surface mining sites and mining waste dumps into a variety of new opportunities, including a horse race track, an in-line skating rink, and an 18-hole golf course. A motor-racing circuit and reservoir for water sports was also developed over a period of years. A canoe park for white-water recreation was created in a former lignite mining site near Markkleeberger See in the Lausitz Lake District in Germany. Adventure courses, including rope structures, swaying bridges, rope swings, pathways, and zip lines, have been developed in industrial facilities such as the former iron and steel factories in Landschaftspark, Duisburg-Nord in Germany, and there is no reason that the same types of outdoor courses could not be designed for former mine sites.

Scale of Restoration Opportunities and Challenges

Scale, in both time and distance, is a major factor in evaluating site restoration. The Pinal Creek Basin of central Arizona is a copper mining area that illustrates some natural attenuation processes, as well as the overwhelming scale of site restoration challenges. Typical of many southwestern United States alluvial basins, the Pinal Creek area is characterized by arid climate. Source mechanisms to receiving streams are controlled predominantly by shallow groundwater flow paths in buried alluvial valleys. Area mining and mineral processing occurred from 1878 to 1970. During that period, the shallow alluvial aquifer had been highly impacted by acid drainage and associated metals contamination. The plume of acidic water extended 15.5 miles (25 km) down gradient from the location of mining operations at the head of the basin (Figure 32.9), and contained excessive concentrations of iron, manganese, copper, zinc, aluminum, cobalt, and nickel.

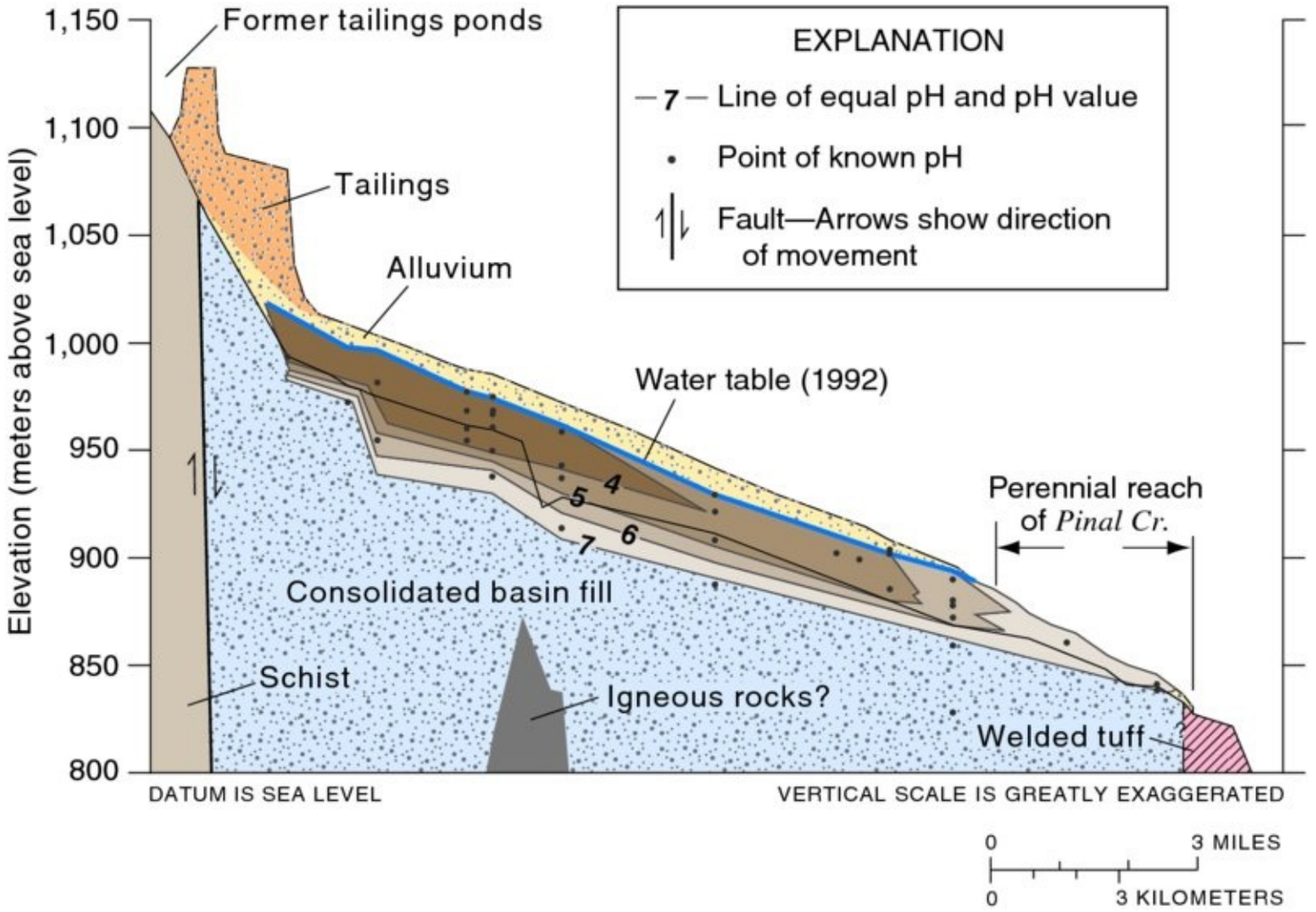

FIGURE 32.9 Cross-section of Pinal Creek Basin showing the pH of the groundwater contaminant plume migrating from the former location of mining and related activities at the far left. (From Bekins et al., 2001, as modified by Stollenwerk, 1994.)

Work by Bekins and others (2001) shows that the source of the plume probably had a pH of 2 to 3 and iron and sulfate concentrations exceeding 2000 and 19,000 mg/L, respectively. Further downgradient groundwater had a pH of less than 4, eventually increasing to a pH of 5 to 6 as carbonate minerals neutralized the acidity. Not surprising, the lowest-pH groundwater corresponds to the areas containing the highest concentrations of dissolved metals. The concentrations of dissolved metals are reduced by sorption onto aquifer solids and precipitation of dissolved metals with increasing pH. Oxidation or sorption of metals in the streambed of Pinal Creek further attenuates metals that reach the perennial stream. Aqueous geochemical conditions from the former tailings ponds downslope to Pinal Creek have been shown to change as carbonate and manganese oxides dissolve pH and calcium in groundwater increases, and away from the ponds, iron, copper and aluminum concentrations decrease in the aquifer. As the groundwater plume migrates through the subsurface, oxidation of dissolved and reduced iron in the aquifer by sediment manganese oxides results in iron precipitation and release of more dissolved manganese. The acidic groundwater reacts with the native carbonate minerals and sorption of hydrogen ions on the precipitated iron increases the pH to 5–6 (Stollenwerk, 1994). The sorption reactions of aqueous copper, cobalt, nickel, and zinc are related to pH. At the location where the pH increases in the acid groundwater, sorption by iron oxides removes substantial quantities of soluble copper from the groundwater and the migration of dissolved cobalt, nickel, and zinc is retarded. The pH increase associated with the carbonates also causes aluminum to precipitate onto the aquifer solids. Metal sorption

reactions are reversible allowing for the remobilization of sorbed metals back into groundwater in areas where pH decreases occur or redox conditions change. Many of these reactions are purely chemical in nature, whereas some reactions involving iron, manganese, and sulfur, for example, can be catalyzed by microbes.

Precipitation of manganese oxides on the Pinal Creek sediments is enhanced by the presence of manganese-oxidizing bacteria, which immobilizes about 20% of the dissolved manganese flowing out of the drainage basin (Harvey and Fuller, 1998). Sorption onto the manganese oxides also reduces the dissolved mass of nickel, zinc, and cobalt in the stream by 12–68% depending on the type of metal (Fuller and Harvey, 2000). Dilution over a 4.3 mile (7 km) perennial reach of Pinal Creek resulted in an additional 20% decrease in concentrations of the dissolved metals. Postmining opportunities and environmental restoration at large acid drainage sites can rely to some degree on similar natural attenuation processes that govern the fate of metals, substantially reducing the mobility of metals in aquifers and streams that receive groundwater impacted with metals. Source control, capping, revegetation, and water control and treatment are common remedies.

Summary

Mining areas are frequently in scenic areas with many resources. Unfortunately, all too often the diversity of the local economies was limited to mining and the support services. Once mining declines or disappears in an area dependent on one industry, as many in mining towns know too well, difficult social and economic issues arise. The examples of postmining opportunities described in this chapter demonstrate the diversity of ideas that have been developed and implemented on a specific basis to address the unique local advantages and strengths of postmining communities. One idea or concept for mine and community restoration will probably not resolve all the social and economic problems of the region. Rather, an integrated and inclusive approach using facilitated meetings with mine owners, government agencies, banks and redevelopment lenders, granting institutions, universities, and the community is the basis of successful long-range planning and implementation of postmining opportunities.

The inclusive nature and collaborative strategies of successful postmining opportunities usually have multiple governmental agencies cooperating with numerous grants and funding sources. Strong local leadership can provide bold vision with significant public input creating multiple strategies and approaches that benefit an entire community. Many of the challenges facing communities with postmining opportunities relate to addressing seemingly unrelated social and economic problems. Actually, many of these challenges are related: the need for sustainable local employment, the desire to offer young people environmental education, the need to retrain unemployed persons in new skills, the desire to share the natural beauty of an area and encourage tourism, the need for resource recovery of minerals and recycling of water, the focus on developing locally grown food, and the ability to optimize the uniqueness and character of a former mining community into an interesting mix of diversified businesses so that economic and environmental success will become a reality.

References and Suggested Reading

American Institute of Chemical Engineers, 2001. Layer of Protection Analysis: Simplified Process Risk Assessment. Center for Chemical Process Safety, AIChE, New York, p. 270.

ASTM International, 2012. New Guide for Incorporating Sustainable Objectives into Cleanup. ASTM WK23495. http://www.astm.org/DATABASE.CART/WORKITEMS/WK23495.htm.

Bekins, B.A., Rittman, B.E., and MacDonald, J.A., 2001. Natural Attenuation Strategy for Groundwater Cleanup Focuses on Demonstrating Cause and Effect, *Eos*, Transactions, AGU, January 30, 2001, 82, 5, pp. 53, 57–58, downloaded February 14, 2014, http://toxics.usgs.gov/pubs/eos-v82-n5-2001-natural/

California Environmental Protection Agency, 2009. Interim Advisor for Green Remediation. Department of Toxic Substances Control, CEPA, Sacramento, CA, 40 pp.

Downing, B., and Mills, C., 2000. Natural Acid Rock Drainage and Its Impact Upon Background Metal Concentrations. Class Notes. EnviroMine, Vancouver, BC, Canada, 18 pp.

Edwards, A.R., 2005. The Sustainability Revolution: Portrait of a Paradigm Shift. New Society Publishers, Gabriola Island, BC, Canada.

Ellis, D., 2005. Remedial selection matrix. Presented at the National Brownfields Conference, May 5.

Ellis, D.E., and Hadley, P.W., 2009. Sustainable remediation white paper: Integrating sustainable principles, practices, and metrics into remediation projects. Remediation, Summer, p. 110.

EUROPA. European Commission website for LCA tools, services and data. http://lca.jrc.ec.europa.eu/lcainfohub/toolList.vm.

Fuller, C.C., and Harvey, J.W., 2000. Reactive uptake of trace metals in the hyporheic zone of a mining contaminated stream, Pinal Creek, Arizona, Environmental Science & Technology, vol. 34, pp. 1150–1156.

Fish, C.L., Hedin, R.S., and Partezana, J., 1996. Chemical characterization of iron oxide precipitates from wetlands constructed to treat polluted mine drainage. In: Proceedings of the 13th Annual Meeting of the American Society for Surface Mining and Reclamation, Princeton, WV, pp. 541–549.

Harvey, J.W., and Fuller, C.C., 1998. Effect of enhanced manganese oxidation in the hyporheic zone on basin-scale geochemical mass balance, Water Resources Research, vol. 34, pp. 623–636.

Hedin, R.S., 1998. Potential recovery of iron oxides from coal mine drainage. In: 19th Annual West Virginia Surface Mine Drainage Task Force Symposium, West Virginia University, Morgantown, WV.

Hedin, R.S., 2002. Recovery of marketable iron oxide from mine drainage. In: Proceedings of the 2002 National Meeting of the American Society of Mining and Reclamation, June 9–13, Lexington, KY, pp. 517–526.

Interstate Technology and Regulatory Council, 2004. Remediation Process Optimization: Identifying Opportunities for Enhanced and More Efficient Site Remediation. Technical/Regulatory Guideline. ITRC, Washington, DC.

Interstate Technology and Regulatory Council, 2011a. Technology Overview: Green and Sustainable Remediation: State of the Science and Practice. GSR-1. Prepared by the ITRC Green and Sustainable Remediation Team, Washington, DC, 84 pp.

Interstate Technology and Regulatory Council, 2011b. Technology Overview: Green and Sustainable Remediation: A Practical Framework. GSR-2. Prepared by the ITRC Green and Sustainable Remediation Team, Washington, DC, 135 pp.

Jacobs, J.A., and Testa, S.M., 2012. Sustainable remediation and green resource extraction practices of

acid mine drainage sites. In: Reclaiming the Sierra: Green Solutions to Abandoned Mines, Sierra Fund, Nevada City, CA, May 3–5. Abstracts, p. 12 of 23.

Jalili, P., Saydam, S., and Cinar, Y., 2011. Co_2 Storage in Abandoned Coal Mines. University of Wollongon Research Online, February 10–11, pp. 355–360.

Johnson, D.B., and Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. Science of the Total Environment, vol. 338, pp. 3–14.

Kairies, C.L., Watzlaf, G.R., Hedin, R.S., and Capo, R.C., 2001. Characterization and resource recovery potential of precipitates associated with abandoned coal mine drainage. In: Proceedings of the Annual Meeting of the American Association for Surface Mining and Reclamation, Albuquerque, NM.

Pearman, G., 2009. 101 Things to Do with a Hole in the Ground. Post Mining Alliance in association with the Eden Project, Cornwall, UK, 138 pp.

Rawlings, D.E., and Johnson, D.B., eds., 2007. Biomining. Springer-Verlag, Berlin, 314 pp.

Reynolds, S.D., 2008. Spenceville Abandoned Copper Mine, Nevada County, California. Draft Final Closure Report. California Geological Survey, Sacramento, CA.

Reynolds, S.D., 2012. Reclamation of Spenceville copper mine. In: Reclaiming the Sierra: Green Solutions to Abandoned Mines, Sierra Fund, Nevada City, CA, May 3–5, Abstracts, p. 17 of 23.

Semmens, K., and Miller, D., 2003. Utilizing mine water for aquaculture. IWC-03-24. In: Proceedings of the International Water Conference, Pittsburgh, PA, October 19–23.

Semmens, K., Delabbio, J., and Eya, J., 2003. Verifying yield at two West Virginia trout farms. In: Proceedings of the National Aquaculture Extension Conference, Tucson, AZ, April 7–11.

Silva, R.D.A., Castro, C.D., Petter, O., and Schneider, I.A.H., 2011. Production of iron pigments (goethite and hematite) from acid mine drainage. In: Proceedings: Mine Water—Managing the Challenges. International Mine Water Association, Aachen, Germany.

Stollenwerk, K.G., 1994. Geochemical interactions between constituents in acidic groundwater and alluvium in an aquifer near Globe, Arizona, Applied Geochemistry, vol. 9, pp. 353–369.

U.S. Environmental Protection Agency, 2008a. Energy Consumption and Carbon Dioxide Emissions at Superfund Cleanups. Draft. U.S. EPA, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. Environmental Protection Agency, 2008b, Green Remediation: Incorporating Sustainable Environmental Practices into Remediation of Contaminated Sites. EPA 542-R-08-002, 56 pp. http://www.cluin.org/download/remed/green-Remediation-Primer.pdf. Retrieved September 17, 2013.

U.S. Environmental Protection Agency, 2008c. Green Remediation: Best Management Practices for Excavation and Surface Restoration. Office of Superfund Remediation and Technology Innovation Quick Reference Fact Sheet. EPA 542-F-08-012, 4 pp. http://epa.gov/tio/download/remed/gr_quick_ref_fs_exc_rest.pdf. Retrieved September 17, 2013.

U.S. Environmental Protection Agency, 2009. Superfund Green Remediation Strategy, Public Review Version. U.S. EPA, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. Environmental Protection Agency, 2012. A Breath of Fresh Air of America's Abandoned Mine Lands: Alternative Energy Provides a Second Wind. U.S. EPA, Abandoned Minelands Team, Washington, DC, 27 pp.

33
SYSTEMATIC LAND RECLAMATION ASSESSMENT AT ACID MINE DRAINAGE SITES

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The legacy of abandoned mines over the past few thousand years has left an inventory of abandoned mine sites worldwide that number in the millions. Many of these abandoned sites have acid drainage issues. The legacy of 150 to 200 years of mining in the United States has left an inventory of thousands of abandoned hardrock mine sites in the West and primarily coal mine sites in the Appalachian mountain areas with no legally responsible parties to pay for cleanup and land restoration related to acid mine drainage.

Perhaps hundreds of thousands of abandoned mine sites exist in the United States, no serious audit has ever been made. (http://www.abandonedmines.gov/ep.html). Of these, over 9600 abandoned mine sites are listed in the Abandoned Mine Lands Inventory System. The inventory includes nearly 1100 abandoned mines in Montana alone (Office of Surface Mining Reclamation and Enforcement, 2008). The Montana offices of the U.S. Bureau of Land Management and the U.S. Forest Service as well as the Montana Department of Environmental Quality AML Program have been working to clean up abandoned mine lands since 1995. In this chapter we describe a systematic approach to assessing the current condition of reclamation work at reclaimed mine sites in the northern Rocky Mountain region. The protocol described was designed as a preliminary assessment tool to evaluate pertinent attributes found at specific locations within a reclaimed mine site (i.e., repository, wetland, etc.).

Introduction

Abandoned mine sites, even within a single state, are quite variable. Many mine sites have mine waste materials with concentrations of metals that constitute a human health hazard. In addition, these contaminants are frequently released into receiving streams and groundwater (U.S. Bureau of Land Management, 2008). Abandoned mines are often located on patented private land, while downgradient mine wastes are deposited on public lands used for recreation, grazing, timber harvest, wildlife habitat, and water resources. Waste materials represent toxicological risks to humans as well as terrestrial and aquatic organisms. In general, state and federal agencies have given priority to sites with mill tailings and waste rock dumps situated in stream channels, and the cleanup of such affected lands on a watershed basis through interagency cooperation has been emphasized (U.S. Geological Survey, 2008).

A common strategy for the cleanup of abandoned sites is to remove waste materials from stream channels, consolidate wastes in on-site repositories, cap wastes with locally available cover soils (generally using some type of a liner), or cap waste materials in place. Mine, mill, smelter, and related structures are sometimes demolished if they are not culturally significant or are unsafe. Mine shafts and adits are backfilled or bat-gated. The purpose of reclamation work on active mine sites as well as abandoned or reclaimed mine sites is to protect human health and mitigate risk to the environment (U.S. Bureau of Land Management, 2008). Restoring and maintaining functioning ecological systems is an overall target for abandoned mine reclamation work. Reclamation activities at abandoned hardrock and coal mines are often complicated, time consuming, and expensive. Specific cleanup goals and objectives are set before

work begins and drive the project through completion. Postreclamation monitoring is required to assure that the initial goals and objectives are still being met, as over time, conditions at a reclaimed site will change. Natural processes may change plant communities, water drainage patterns, and other attributes of a reclaimed site. These processes are normal and to be expected; however, if reclamation activities are affected negatively, a site that once appeared to be functioning as planned may deteriorate. Examples include undesirable plant species moving into a reclaimed site and disrupting the natural succession of the intended plant community, or gullies forming on recontoured slopes due to erosion caused by storm water runoff. Generally, these types of negative site conditions worsen over time.

The overall objective for developing the procedures described here is to provide a common method to evaluate and monitor reclaimed mine sites. Routine on-site evaluations of the current condition of reclaimed sites is paramount to assuring that past reclamation activities are still meeting the initial goals and objectives and, if not, identifying conditions that need attention. Identifying problem areas early typically results in the remedy being less complicated and expensive than allowing the deteriorating conditions to persist and probably worsen. Attributes that might be assessed at a reclaimed site include vegetation cover, erosion control, status of a cap or liner, road condition, evidence of acid mine drainage, and more. The data and information collected during a qualitative land reclamation assessment can then be used to evaluate the status of the reclamation work and whether or not the conditions at the site remain protective of human health and the environment. If conditions at the site have declined, this preliminary site assessment will trigger maintenance activities.

The preliminary reclamation evaluation process described here was designed to be qualitative so that assessments are cost-effective (no expensive equipment or laboratory analyses), completed in a timely manner, and give the responsible party an overall picture of conditions at the site. If the findings from the preliminary assessment determine that there are areas at the reclaimed site that need maintenance, a more in-depth assessment may be conducted. Depending on site conditions, quantitative site evaluations may be needed to determine the extent of the issues. These evaluations are sometimes referred to as phase II site evaluations and may include soil, vegetation, and/or water sampling, geotechnical testing, or other quantitative investigation methods. This information is then used by the responsible party to develop a site maintenance plan.

Systematic Reclamation Evaluation and Monitoring Program

There is developing interest on the part of federal agencies to begin monitoring reclaimed mine sites in a systematic way (U.S. Geological Survey, 2008). Evaluating reclaimed mine sites using a common method of standard evaluation forms (with site-specific features noted) assists federal and state agencies responsible for risk management and land management in accomplishing their respective missions. Communication within and among agencies is made easier when all parties use similar methods for collecting data. There are four desired outcomes from instituting a systematic reclamation evaluation and monitoring program.

1. Identify when and where there is a need for maintenance on a reclaimed site. It is important to ensure that reclamation work performed remains protective of the resources and that human health risks are reduced.
2. Provide temporal information that will allow trend analysis of cleanup status.
3. Identify cleanup methods and technologies proven to be effective and identify those that have resulted in poor performance.

4. Provide agencies with data and information that can be used to support their ongoing remediation programs.

Another goal of the systematic approach is the sharing of information among agencies and other interested parties. If the agencies and others involved in these evaluations use the same assessment forms, it makes it possible to create a database that can be shared among interested parties. Standardized electronic data collection forms make it possible to download findings directly into a database. The database can then be queried, updated, and shared by interested parties. Standardized questions and answers are required with the exception of “comment” fields. The downside of this approach is that it is more difficult to incorporate special conditions at a site. However, this can be addressed by creating an additional electronic form for the special condition at the site and adding the information to the database by creating a new table.

Objectives

The overall objective of a systematic reclamation evaluation and monitoring program is to provide a tool that is a straightforward, easy-to-apply on-site method and results in standardized data that reflect the current condition of the site, including. Using the data collected during the on-site evaluation, land managers and the public can have the information necessary to determine if remedial objectives continue to be met, or if maintenance is necessary. Described below are the field forms used to collect data related to the current condition of the reclamation work so that issues such as address public safety, revegetation success, erosional stability, and other issues related to reclamation activities can be addressed. Once data have been collected and reviewed, it is possible to determine if maintenance is necessary. If maintenance is necessary, the data are used to plan future activities such as what and where maintenance is necessary and if addition data are needed for the maintenance plan. If multiple years of data have been collected, it may possible to determine trends in the condition of specific attributes at the site.

Site-Specific Field Inspection Forms

The field inspection forms include observations that are supported by field notes, maps, drawings, photographs, global positioning system (GPS) coordinates, and other information that relates to the following topics:

- Public safety and maintenance
- Mine waste repositories
- Waste rock dumps
- Removal areas
- General remediated areas
- Wetland areas
- Streambank/riparian areas
- Adits and shafts
- Borrow areas
- Summary of evaluated areas

If sharing information among agencies and interested parties is a goal of the reclamation evaluation, it is recommended that standardized questions be used on the forms so that all data can be collected

electronically in the field and downloaded into a central database. However, field inspection forms prepared by agencies or environmental professionals can be made for each topic listed above based on the history of the mine and property. The field inspection forms contain multiple questions and checklists regarding relevant features that are found at specific locations within a reclaimed mine site, such as repositories, wetlands, waterways, and removal areas. The attributes of the features may include vegetation cover, the status of a cap or liner, roads, the erosion status, evidence of acid mine drainage, weed infestations, and more. The responses are qualitative in nature and agency personnel can be trained to (repeatedly) provide the required information accurately and precisely, supported by digital photographs and other field observations and documentation. Various types of feature-specific field inspection forms are summarized below.

Public Safety and Maintenance

Public safety is one of the driving forces behind reclaiming abandoned mine sites. These areas are often visited by people interested in the history of mining in the area or may easily be accessed for such recreation activities as off-road vehicle driving. Safety issues range from physical dangers, such as open adits or dilapidated structures, to exposure to hazardous waste materials. Public safety issues at reclaimed mines include identifying whether a safety issue requires immediate maintenance or routine maintenance. The public safety and maintenance evaluation is an assessment of the entire site. Site attributes might vary for specific mine properties in a specific region; consequently, if several properties are being evaluated, the project designer should develop a standard evaluation checklist for the project area. The development of a standardized mine evaluation form for a project area (which might include dozens of abandoned surface as well as subsurface mines, waste piles, etc.) should include prompts and checklists to address a variety of mine-related features and environmental conditions. For example:

- Fences, gates, signs
- Roads, culverts, bridges
- Erosion geotechnical
- Adits and shafts
- Fire
- Waste repositories
- Monitoring wells
- Exposed waste materials
- Historical structures
- Surface waters
- Land-use issues
- Weeds
- Storm water control
- Site boundaries

Using a public safety and maintenance evaluation form also prompts the evaluator to determine the degree of urgency related to the maintenance issues. Is the problem such that it can wait until the next routine maintenance trip is scheduled for that site, or does it require immediate attention in order to protect human

health and the environment? Figures 33.1 and 33.2 document aspects related to site-specific public safety using this evaluation method at the mine sites inspected.

FIGURE 33.1 Gated adit protecting public safety; untreated water is a source of acid mine drainage.

FIGURE 33.2 Dilapidated historic structure poses a risk to public safety.

Mine Waste Repositories

A mine waste repository is an engineered disposal cell similar to a landfill (Ford and Walker, 2002). Many abandoned mine cleanup activities include the construction of a repository either at the site or nearby. Design of a repository depends largely on site conditions but should remain stable in the long term and prevent migration of contaminants into the environment (Lottermoser, 2003). Repository concerns include vegetation community and cover, condition of diversion structures, drainage or seepage, erosion, and stability, including signs of slope failure or subsidence. Repositories may be located away from the abandoned mine site, therefore the evaluators must be knowledgeable of the locations of these repositories. Figure 33.3 shows a mine waste repository with poor vegetative cover, promoting erosion.

FIGURE 33.3 Repository with poor vegetation cover and rills and gullies caused by erosion.

Waste Rock Dumps

A waste rock dump is typically a historic pile of overburden that may be environmentally innocuous or contain contaminated materials and produce runoff water of poor quality. Waste rock dumps are generally not highly engineered; rather, unwanted rock (rock of low economic value) was simply dumped in a convenient location that often included steep slope areas. The type of reclamation work occurring on waste rock dumps is variable and can range from no action to installing a constructed cap. Figure 33.4 shows waste rock and other mine-related materials that were dumped down a steep slope.

FIGURE 33.4 Waste rock and other material were dumped down the side of a steep slope. Erosion and surface water runoff quality are of concern at this site.

Removal Areas

Removal areas are common on reclaimed mine sites and may include areas where tailings, contaminated soil, waste rock, or other contaminated material has been removed. These areas are generally covered with borrow soil and revegetated, but not always. Several attributes are assessed in removal areas; examples include vegetation community, remaining waste, erosion, exposed tailing material, water diversion features, acid mine drainage, metal salts, seeps, and impacts of and to adjacent land. Figures 33.5 and 33.6 show waste material left in place and poor vegetation establishment in a removal area, respectively.

FIGURE 33.5 Waste material left in place adjacent to a removal area. Run-on from the contaminated area is affecting the reclaimed area.

FIGURE 33.6 Poor vegetation establishment in removal area.

General Remediated Areas

General remediated areas are reclaimed areas within a site that are not assessed using the other feature-specific evaluation forms. Some examples include areas of in situ remediation or possibly a construction-related staging area. These areas may have been treated in place, graded, revegetated, or experienced other reclamation activities. This form asks the evaluator to assess attributes that include, but are not limited to; vegetation community, erosion, weeds, instability of slopes, acid mine drainage, exposed waste, and impact of or to adjacent land. Figure 33.7 shows an area that was treated using in situ remediation methods.

FIGURE 33.7 Area treated using remediation in place (in situ). Lime and organic matter were tilled into the contaminated soil and the area was revegetated.

Wetland Areas

Wetland areas may be original to the site or may have been constructed as part of the reclamation design. Assessment attributes include looking at the seasonal water level of the wetland, determining if acid drainage discharges into the wetland, checking plant community health, sedimentation, water diversion features, and more. Figure 33.8 shows a wetland in a reclaimed area.

FIGURE 33.8 Wetland in a reclaimed area; the silt fence needs maintenance or removal, depending on the erosional characteristics of the adjacent area.

Streambank/Riparian Areas

Many reclaimed mine sites have small streams running through the area, and these waterways are generally affected to some degree by mining activities. Assessing the condition of reclamation work on streambanks and/or riparian areas is important because these areas can degrade rapidly if problems arise. Attributes evaluated at streambank/riparian areas at reclaimed sites include vegetation community and health, lateral cutting of streambanks, evidence of acidic drainage, exposed waste, sedimentation in waterways, and impacts on or from adjacent land. Figures 33.9 and 33.10 show acid mine drainage discharging into a clear stream, and dead and dying streambank vegetation, respectively.

FIGURE 33.9 Acid mine drainage discharging into a clear stream. Notice that vegetation is poorly established on the streambank near the acid water.

FIGURE 33.10 Dead and dying streambank vegetation in a reclaimed area.

Adits and Shafts

Abandoned mine sites require the closure of unsafe mine adits and shafts. These mine features can pose a serious risk to the public. Additionally, adits and shafts commonly discharge water from old mine workings. Assessment attributes include the condition of the water being discharged, the path of the discharged water, and the condition of the device used to close the adit or shaft. Figures 33.11 and 33.12 show a temporarily closed mine shaft and mine adit closure, respectively.

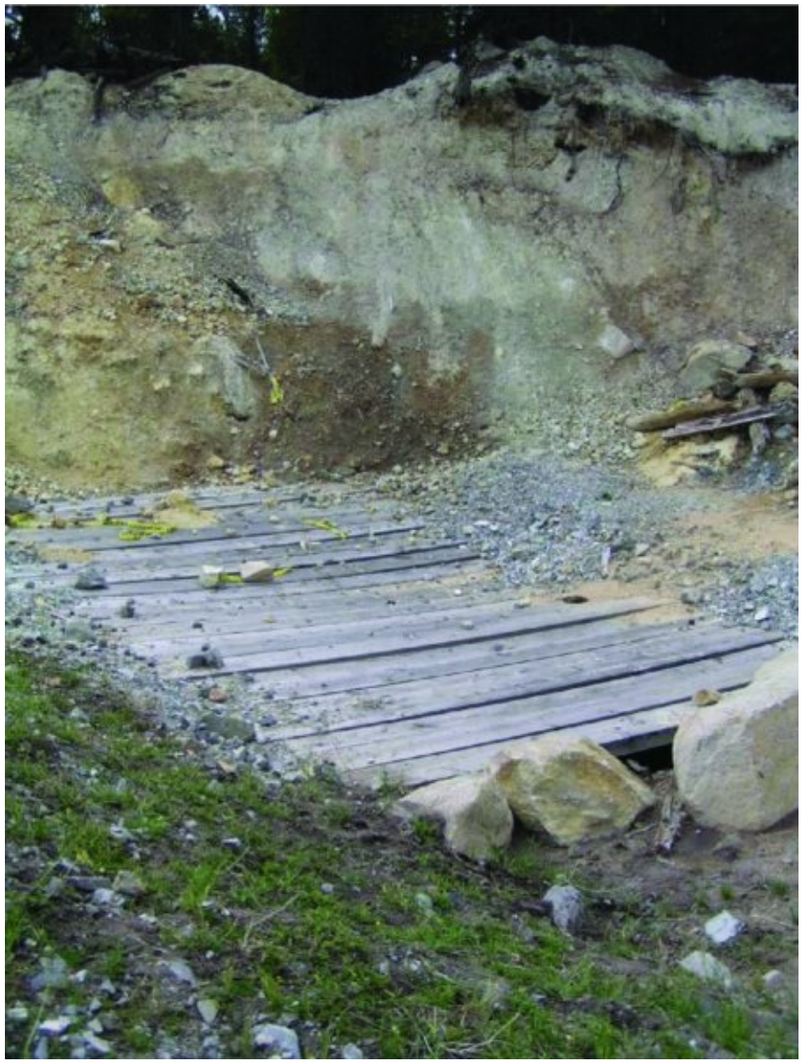

FIGURE 33.11 Temporarily closed mine shaft.

FIGURE 33.12 The mine adit closure bulkhead at this reclaimed site is located several feet inside the opening, creating an attractive nuisance and a risk to site visitors.

Borrow Areas

Borrow areas are locations where uncontaminated soil or fill material was removed, creating a pit that generally requires recontouring and revegetation. Borrow sites may be located some distance from an abandoned mine site. In some cases following removal of borrow material, the pit may be used as a repository. Attributes addressed at borrow areas include vegetation conditions, erosion characteristics, impacts of or to adjacent land, water diversion features, and slope stability. If the pit was filled with waste material, the borrow pit would then be assessed using the repository or waste rock dump form. Figure 33.13 shows a revegetated borrow area.

FIGURE 33.13 Revegetated borrow area.

Summary of Evaluated Areas

The final field inspection form is used to summarize the results of on-site reclamation evaluation. This information is then used for the final evaluation report.

Conducting an Evaluation

Prefieldwork Preparations

Before the site visit and actual fieldwork begins, field assessment packets are assembled for each remediated abandoned mine site to be assessed. If possible, this packet of information includes the following: a construction completion report, as-built drawings, construction change orders, and any maintenance work completed after initial remediation. If these documents are not available, the construction bid documents can be helpful in gaining an understanding of the remediation activities that were to be completed. Hard-copy maps of the site, recent aerial photos, and any graphic information system (GIS) files should also be included in the packet. If a person familiar with the work that occurred at the site is available for an interview, it is recommended that the evaluator contact that person and discuss the site and implementation of remedial or reclamation actions. The evaluation forms mentioned above are used during field assessments. Any issues related to access onto private property need to be

resolved prior to entry by evaluators. Written access agreements may be required and should be part of the packet.

Evaluator Qualifications and Training

Evaluation of these sites is based on a range of qualitative estimates and observations from simple physical attributes to complex ecological associations (e.g., estimating the percent canopy cover within a plant community). Therefore, training in the use of the field inspection forms is required. The purpose of the training is to achieve precise (repeatable) assessments by evaluators. Training at selected field sites should be conducted on a regular and continuing basis to help calibrate the evaluator's qualitative estimates of site conditions. Evaluators should have a knowledge of basic science, engineering, and ecology. Some knowledge of ecological and environmental field measurement methods, as well as land reclamation techniques, is required. Field experience in range condition assessments, vegetation community measurements, geology, soil remediation, phytotoxicity, and evaluations of erosion is desirable. Persons with bachelor of science degrees in land rehabilitation, range science, or soil science typically have acceptable combinations of experience and knowledge.

Initial Field Assessment

Evaluations should be conducted during the optimal phenological time for seeded plant species, which is generally between mid-June and mid-September for most abandoned mine sites in the northern Rocky Mountains. When scheduling site visits, evaluators should consider the location, including the elevation, of the reclaimed sites. Snow cover will take longer to melt at high-elevation locations. A preliminary walkthrough of the entire remediated site is performed to:

1. Confirm boundaries of the remediation.
2. Ascertain and/or confirm the locations where various reclamation techniques were implemented.
3. Identify locations of historical features, creeks, repositories, adits and shafts, wetlands, and other features specific to the remediated site.

The site is then assessed for public safety and general maintenance. This field inspection form asks questions in 13 categories and stresses issues relating to public safety and the need for routine or immediate maintenance to protect human health and/or to protect remediated landscapes. The public safety and general maintenance field inspection form is an assessment of the entire site; additional evaluation forms are used by the inspection team to evaluate specific reclaimed features within the site. After a public safety and general maintenance field inspection form is completed, with appropriate notes, digital photographs, and GPS coordinates recorded, a summary of the findings is completed.

Documentation

Field documentation should be detailed and verify and support the observations in the field. Photographic documentation of the reclaimed sites is required. During evaluation of the site, GPS coordinates mated with digital images are required when problems are encountered, especially those that may constitute a public safety or critical maintenance issues. Digital images should also be used to document overall site conditions; during the first site visit, at least two permanent photo points should be established. Permanent photo points can be used to represent conditions at the site over a multiyear period. An overview perspective of the entire site is preferred for the permanent points. Images captured in subsequent years should be matched to the same field of view.

A camera that has an embedded GPS unit or some type of wireless connection with a GPS unit is extremely helpful when taking digital photographs. Photos with GPS coordinates can be downloaded into the database along with the data collected in the field. This results in having all of the data in one location. A dry erase board with date, location, and comments can be included in the photos of features. The board can also be used to index field photos and notes to images downloaded from the digital camera. An electronic file naming convention is recommended for downloaded images to match year, site, and feature.

Evaluations of Site-Specific Features and Areas

As summarized above, site-specific features of a remediated abandoned mine may include waste repositories, constructed wetlands, adit discharge channels, removal/replacement areas, treated areas, reconstructed streambanks or channels, and other remediated locations. Feature-specific evaluation forms were discussed previously in this document. In general, these forms ask questions pertaining to landscape stability, vegetation integrity, water quality, and evidence of adverse impacts of the remediation on adjacent lands. At the end of each form, a narrative of feature-specific problems, associated digital photos, and GPS coordinates is recorded. A new form is used for each feature. For example, if there are two repositories at the site, a separate field form should be completed for each repository. In the field notes, feature-specific problems are identified that may inhibit the long-term effectiveness and permanence of the remediation.

Site Sketch or Map

A depiction of the location and areas evaluated is required. Recording points, polygons, and lines using a GPS unit is ideal for identifying areas of interest on postassessment maps. However, a site sketch may be acceptable. The preferred map for the site visit is an electronic aerial photograph downloaded onto a GPS unit. Points, polygons, and lines can then be recorded in the field using GPS/GIS technology. A printed recent aerial photograph can be annotated to depict areas evaluated if necessary. If possible, each area evaluated should be marked or sketched on the aerial photo.

Reclamation Evaluation Reports

A reclamation evaluation report should be prepared for each site, and at a minimum each report should contain the following:

- A narrative of findings which includes identification of any immediate threats to public safety, identification of high-priority maintenance needs to protect the remediation, and a synopsis of the comments and field notes
- Completed field forms, preferable downloaded from the database and presented in a tablular format
- Digital photos and GPS coordinates of problem areas
- Maps and current aerial photos used in the field to depict boundaries of site-specific features (e.g., repositories, wetlands, removal areas)
- Historic aerial photos showing previous activities

Summary

Developing a systematic reclamation evaluation protocol provides a common method to evaluate

reclaimed mine sites so that agencies responsible for land and risk management can communicate easily and work in partnership with the public and stakeholders to accomplish their respective missions. The data and information collected during a reclamation assessment can be used for trend analysis and to evaluate the status of the reclamation work and whether or not the conditions at the site remain protective of human health and the environment. Another advantage of reclamation monitoring is the ability to identify cleanup methods and technologies that are proven to be effective and to identify those that have resulted in poor performance.

Problems and Questions

1. Explain why abandoned lands might create problems for the U.S. Bureau of Land Management.
2. Who is financially responsible for environmental impacts from abandoned mines located on public lands?
3. Regarding acid mine drainage, what might be the value of a historic aerial photo that might not be seen on a current aerial photograph?
4. Name the advantages of a systematic approach to land reclamation assessment.
5. State at least three objectives of an initial field assessment.
6. What value would GPS provide researchers taking photographs of vegetation and hillside erosion?
7. What policies and regulations might be developed to better protect public and private lands from the unintended impacts of acid drainage?
8. Can acid drainage occur on lands not associated with mining activities?

References and Suggested Reading

Bitterroot Restoration, Inc., 2004. Clark Fork River Riparian Evaluation System, Clark Fork River Operable Unit, Milltown Reservoir Sediments NPL Site. Prepared for CH_2M Hill and U.S. Environmental Protection Agency, Region VII, Montana Office, by Bitterroot Restoration, Inc., and Reclamation Research Unit, Montana State University, Bozeman, MT.

Blicker, P.S., Neuman, D.R., and Jennings, S.R., 2009. In: Revitalizing the Environment: Proven Solutions and Innovative Approaches, National Meeting of the American Society of Mining and Reclamation, Billings, MT, May 30–June 5, R.I. Barnhisel, ed. ASMR, Lexington, KY.

CDM, 1999. Preliminary Draft: LRES Phase II Report Preliminary Land Reclamation Alternatives. Document 3289-001-RT-OTHR-04850, U.S. Environmental Protection Agency Publication, ARWW&S Operable Unit, Anaconda Smelter NPL Site, Helena, MT. Prepared for EPA by CDM, Helena, MT, and the Reclamation Research Unit, Montana State University, Bozeman, MT.

CDM, 2003. Final Draft: Butte Reclamation Evaluation System, Priority Soils Operable Unit, Butte, Montana. Prepared for EPA by CDM, Helena, MT, and the Reclamation Research Unit, Montana State University, Bozeman, MT.

Ford, K.L., and Walker, M., 2002. Abandoned mine site repositories, site selection, design, and costs. In: Tailings and Mine Waste '02: Proceedings of the 9th International Conference on Tailings and Mine

Waste, January 27–30, Fort Collins, CO.

Lottermoser, B., 2003. Mine Wastes: Characterization, Treatment and Environmental Impacts. Springer-Verlag, New York, 277 pp.

Office of Surface Mining Reclamation and Enforcement, 2008. Abandoned Mine Lands Inventory System website. OSMRE, U.S. Department of the Interior. http://www.osmre.gov/aml/AMLIS/AMLIS.shtm.

U.S. Bureau of Land Management, 2008. Abandoned Mine Lands Portal website. Bureau of Land Management, U.S. Department of the Interior. www.abandonedmines.gov.

U.S. Geological Survey, 2008. USGS Abandoned Mine Lands Initiative website. USGS, Reston, VA. www.amli.usgs.gov.

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RESOURCE RECOVERY

STEPHEN M. TESTA

Resource recovery is the collection and separation of certain waste materials for processing into new forms. Considering that mine tailings and associated waste materials typically account for over 90% of materials extracted during the mining of metals, resource recovery is a means to reduce the amount of waste generated while producing a commercially viable product, or producing a product or material that offsets the cost of purchasing or importing such materials. The U.S. Environmental Protection Agency (EPA) has estimated that between the years 1910 and 1981, an estimated 31 trillion kilograms of mine waste and 13 trillion kilograms of tailings were generated (U.S. Environmental Protection Agency, 1991). Over 80% of the overburden and tailing wastes were estimated to be generated by the mining of phosphate rock, uranium, copper, and iron ore. Resource recovery can play a very important environmental role because it reduces the amount of waste generated, conserves natural resources, minimizes or removes adverse environmental conditions, and is cost-effective.

Introduction

In the reclamation of mine sites, two fundamentally different approaches exist: reclamation and remediation. The primary difference is that *remediation* includes such options as containment, monitoring, avoidance and hazard minimization, and in some cases, no action at all. However, remediation is not reclamation. When considering *reclamation*, the hazard is removed and the resulting mine site condition made suitable for its intended end use, and no hazards remain. Regardless, a major consideration when formulating a reclamation or remedial action plan is what technology will best serve the specific project needs. No two projects are exactly alike and each has site-specific limitations. However, three objectives must always be met for any remediation project to be successful. The approach needs to be environmentally sound, time efficient, and cost-effective.

Reclamation, Reuse, and Recycling Overview

The extraction of Earth's material wealth generates waste rock, soil, and materials that could be deemed hazardous or toxic, and potential or anticipated conditions for acid rock drainage and acidic soils. Resource recovery concepts do not view discarded materials as waste products but as a resource of beneficial use and commercially feasible. Commercial success is marked by the development of a product that can be used to mitigate or contain hazardous conditions, or use of the waste material as an ingredient to produce a valuable product. Given serious thought, there is not much that cannot be reused or recycled in some manner. Disposal or left-in-place strategies should require rigorous review and be limited to materials that cannot demonstrably be reclaimed, reused, or recycled.

Concepts pertaining to recycling, reclamation, and reuse require some clarification. *Recycling* is the use, reuse, or reclamation of all or part of a hazardous material. *Reclamation* involves strategies or approaches that result in the removal of a contaminant from its matrix for the purpose of collection and reuse. Reclamation is not avoidance or minimization of a hazard. In other words, the development of a closure plan with continued monitoring of contaminated groundwater quality in an open-pit metallic mine

for perpetuity may be acceptable within certain states and certain site conditions, but this approach is not reclamation. *Reuse* strategies or technologies involve the incorporation of the contaminant and its matrix as an ingredient to produce a commercially viable product. Contaminated soil being incorporated into an asphaltic end product is an example of reuse. Reuse does not include removal of the contaminant from its matrix or modification of the contaminant.

When considering mining and mineral wastes, waste rock and mine tailings have been used for recycling for asphalt pavement, with limited or experimental use as base rock or embankments and for other purposes. In most cases, further research with consideration of design is required, and performance criteria need to be taken into account. The most attractive and commonly used approach is incorporation of the waste rock and mill tailings as an ingredient to produce an asphaltic product. About 925 and 470 million metric tons have been incorporated into hot-mix asphalt on an annual basis (Kandhal, 1993). The U.S. Department of Transportation was reported by Kandhal (1993) to be using a hot-mix asphaltic product incorporating waste rock in one state, and seven states used the resulting product incorporating mill tailings. Hot-mix plants are stationary; thus, this approach is limited by the availability of stationary hot-mix plants. Incorporation of mine waste using mobile cold-mix plants provides more options in the reuse and recycling of mine wastes and remains greatly underutilized.

Asphaltic Incorporation of Contaminated Soils, Mining Wastes, and Tailings

Reuse and recycling of hydrocarbon-affected impacted soil via incorporation of petroleum-contaminated soils into a commercially successful asphaltic product began on a large scale during the 1990s. Initially, use of this technology was limited to petroleum hydrocarbons, but during the 1990s, use of this resource–recovery oriented technology for the reuse and recycling of metal contaminated soils and waste gained interest in the environmental and remediation community. Notably, lead was claimed to be the most common contaminant encountered at Superfund sites across the United States, but other contaminants of interest included zinc, iron, and arsenic, and in the context of acid rock drainage, any contaminant that could pose an environmental threat to the environment.

The incorporation of contaminated soil and tailings into a commercial asphaltic product is discussed next. A comprehensive treatment of this subject matter is that of Testa (1997). Several methodologies are available for the remediation of metalsaffected material, including extraction, solidification or stabilization, vitrification and electrokinetics. When considering asphaltic incorporation, we have environmentally processed asphalt (EPA), environmentally processed asphalt–second generation (EPA-II), or asphaltic metals stabilization (AMS), depending on the contaminant of concern (i.e., petroleum hydrocarbon–affected soil, previously processed asphalt, and lead- or metals-affected soil, respectively). We will focus here on AMS, which has been shown to be an environmentally sound, time-efficient, and cost-effective process whereby in lieu of a hazardous or toxic waste, an end product for a variety of uses is produced. AMS methodology utilizes contaminated soil as an ingredient in an industrial process to produce a commercially feasible product. Affected soil is incorporated with water-based asphalt emulsion and varying amounts of aggregate to produce a range of cold-mix asphaltic product that fulfills the requirements of a variety of end uses. Notable among these end uses are haul roads, parking areas, subbase, dikes and containment structures, caps and liners, and dust abatement.

AMS has been applied successfully to a variety of site conditions. Metals-affected soil has been fully encapsulated, fixated and solidified, stabilized in a cold-mix asphaltic endproduct via AMS, and demonstrably deemed nonhazardous and regulatory exempt. Consideration of certain engineering and

environmental factors suggests that cold-mix asphalt incorporation of lead and other metals-affected soil will perform more than adequately under normal conditions for a long period of time. Methodology and certain engineering and environmental properties of AMS pertaining to durability, stability, chemical resistance, aging, biological resistance permeability, leachability, chemical aspects, and product use are discussed below.

Resource Recovery Concept

The production of asphalt is conventional in nature and weIl established. AMS is viewed as environmentally sound and has proven to be cost-effective while providing the minimal amount of long-term liability in comparison with other soil remediation options and alternatives. Affected soils, including tailings and mine wastes, which may initially be classified as hazardous waste, are incorporated with asphalt emulsion and specified grades of aggregate to produce a range of cold-mix asphaltic products that fulfill the requirements of a variety of end uses.

Methodology

The incorporation of metals-affected soils to produce a commercial product can be accomplished utilizing one of two processes: mixed-in-place for large-quantities and windrowing for smaller quantities. For large-quantity projects, mixed-in-place is conducted using a portable asphalt batch plant. Providing production averaging 150 tons of cold-mix asphalt per hour, the plant operation consists of a mechanical screening plant, transfer conveyor, electrical generator (all equipment except the rolling stock is electrically powered), asphalt plant or pug mill, and asphalt emulsion truck (Figure 34.1).

FIGURE 34.1 Mobile cold-mix asphalt pug mill with a mobile water-based emulsion truck in the background. Cold-mix asphalt incorporating contaminated soil is being stockpiled in front of the pug mill.

Materials are introduced to the process through the screening unit, which serves to separate all deleterious materials (i.e., trash, plastic, large rocks, etc.) from the soil, and to size material in accordance with the design criteria (Figure 34.2). For example, asphalt subbase would use 1½-in. aggregate, whereas pavement may call for ⅝ in. minus. From the screen, the materials travel on the transfer conveyor to the batch plant's soil hopper. There are two hoppers in the plant unit: one for soil and the other for aggregate. These materials are fed at a predetermined rate from each hopper by variable-speed conveyors and adjustable feed gates. Mix design such as 50% soil and 44% aggregate are maintained to within 1% of total mix. The feed hoppers discharge onto the plant unit's transfer conveyor to the mixing chamber. The materials discharge from the conveyor into a fluffer wheel compartment, where they are mixed further. Inside this compartment the asphalt spray bar applies the required amount of emulsion.

FIGURE 34.2 Lead-affected soil stockpiles ready for incorporation into cold-mix asphalt.

Cold-mix asphalt is produced utilizing a water-based asphalt emulsion. Emulsification of asphaltic bitumens is the process of mixing water with an emulsifying agent (i.e., on the order of dishwashing detergent), and subsequent milling and blending with asphalt bitumens to produce a bituminous product. This product is most commonly known as *water-based asphalt emulsion*. While the manufacture of this product differs greatly from that of hot-mix asphalt bitumen, its use is prevalent, particularly by country road departments. The use of water-based emulsified asphalt is thus encouraged since standard "cut-back" asphalts contain petroleum distillates that volatilize when heated, which illustrates that cold-mix asphalt technology has often been overlooked. Water-based asphalt emulsion utilizes water and emulsifiers to separate and suspend asphalt bitumen molecules in a form that will readily mix with and coat the aggregate materials. Conversely, cut-back asphalts use a range of solvents to perform this function.

From the asphalt compartment the material discharges into the mixing chamber. Inside this chamber are two counter-rotating paddle wheel mixers that have adjustable rotating speeds. This provides the proper retention time to ensure a complete blending of all materials. The product is then transferred into trucks or to a stockpile ready for use. The product can be stockpiled for months until a need is acquired. For smaller quantities, windrowing involves coating the soil with a proprietary emulsion and mixing the materials in place.

Cold-mix asphalt is in very widespread use, due to its versatility. To illustrate, one simply has to ask what type of asphalt is utilized in areas where there are no hot-mix plants or when the economics, and more important, the end use required of the asphalt product, inhibit the use of hot mix. A large part of this versatility is the ability of water-based emulsified asphalt to remain workable for a long period of time. Only upon the force of compaction, which drives out the water and allows the bitumens to come into contact and chemically "break" or bond, will the asphalt product cure or set up (Figure 34.3).

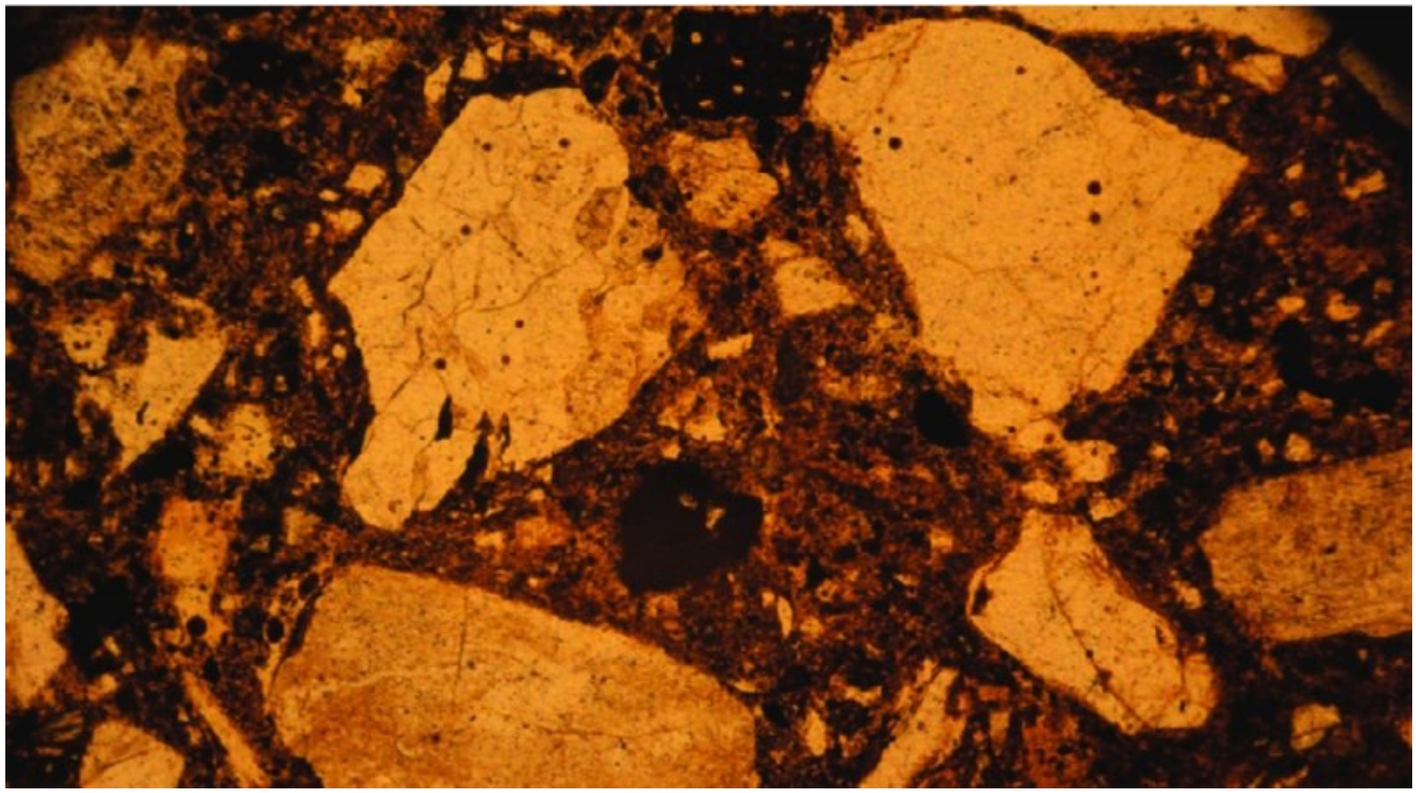

FIGURE 34.3 Petrographic thin section of asphaltic end product, showing aggregate and asphaltic binder.

Unlike conventional hot-mix plants, a portable asphalt plant requires no dryers or heaters, which eliminates “fugitive dust” and emissions, which the general public always associates with asphalt. Further, no petroleum distillates are utilized in cold-mix asphalt emulsion. Cold-mix asphalt production can best be termed environmentally processed asphalt. The common name for asphalt is *asphaltic cement*, as the bitumens, once they “break” chemically , cement themselves together, forming a hard, virtually impermeable mass. This chemical process and the resulting durable mass comprise the essence of the asphalt industries' existence. Simply, asphaltic bitumens held in suspension by emulsifiers or petroleum distillates, when mixed with aggregate, provide a stable, durable surface that is resistant to wear and erosion, which, in turn, makes them an excellent roadway material.

Unlike AMS production, the use of petroleum distillates of three types is essential in hot-mix asphalt products. Hot-mix asphalt is known as *cut-back asphalt* because hot-mix bitumen is cut back with solvents or with kerosene or diesel range distillates. Three grades of cut-back asphalts exist: rapid cure, (RC), or medium cure (MC), and slow cure (SC). These designations relate to the time required for the bitumens to break chemically or to bond and cure. RC cutbacks contain solvents on the order of Stoddard solvents and, as the name implies, cure very rapidly. Hot-mix aggregate is preheated to 180 to 220°C and when compacted, the resulting heat volatilizes the cut-back solvents and the material cures or sets up very rapidly. As a point of interest, the greaater the distance from the hot-mix plant, the slower the hot-mix asphalt is designed to cure, hence the need for variable curing specifications of hot mix (i.e., RC, MC, and SC).

Cold-mix asphalt is a very common, commercially specified, product. Unfortunately, the general public equates “asphalt” with freeways made of hot mix. Cold-mix asphalt differs not in strength and stability, but in preparation aspects, application, compacting, curing, and to some extent, finished appearance. In short, cold mix looks different from hot mix; it is brown and takes longer to cure since it is emulsified with water rather than with petroleum distillates. The fact that the processed asphalt is temporarily brown

is typical of all asphalt products. When refined to first-stage asphalt bitumen, crude oil is always brown. Lampblack or other color is added to hot-mix bitumens to provide a uniform color. Without color added, the highways would be a checkerboard of colors from dark brown to tan, as each batch of asphalt bitumen produced by each refinery is a different color. Color in cold-mix asphalt is added after the material is applied and allowed to cure by way of seal coating. Adequate curing prior to seal coating is very important for cold-mix asphalt utilizing water-based emulsion. There are only two places for the water to escape, as water does not volatilize (as do petroleum distillates) at ambient temperature. The water must escape from the surface by evaporation or be absorbed into the base. If cold-mix asphalt is sealed before it is cured properly (i.e., the water allowed to evaporate), it probably will not cure, as the seal coat prevents evaporation and the water collects under the seal coat in the form of condensation. Seal coating of cold-mix asphalt is an industry standard procedure and in addition to improving wearing properties, it provides the vital appearance factor of being a uniform black color. Normally, this is 7 to 10 days. Hot mix, if opened to traffic too soon, will display the same tendencies as cold mix, such as the development of ruts, and is soft until it cures.

Performance

In viewing the overall and anticipated performance of an asphaltic product, the criteria considered include durability, stability, chemical resistance, aging, biological resistance, permeability, leachability, chemical aspects, and product use.

Durability

The best indicator for considering asphalt in stabilizing and incorporating metals-affected materials is in the use of asphalt for liners, caps, and containment barriers. Asphaltic liners and structures have long-term durability, and performance is easily demonstrated by the existence of surviving asphaltic structures from antiquity. Asphalt was in general use in Western civilizations from about 2000 B.C. to the first century A.D., where its use was superceded by more economical methods of working wood, tar, and pitch, and the exhaustion of deposits available to existing mining technologies. Surprisingly, the ancient mixes are not that dissimilar from modern mixes. Besides the obvious uses as mortars, pavements, revetments, and foundations, in many Mesopotamian sites asphalt liners were commonly used in drainage, water tanks, and plumbing fixtures in thicknesses from 0.1 mm to several centimeters. In many of these cases, the asphaltic structures that have escaped intentional or accidental destruction are still performing their primary function adequately. Samples taken from these structures often show favorable properties, including low permeability, but it is not possible to determine how long exposure to ultraviolet light and surface conditions have affected the asphalt relative to the general aging processes expected in a subsurface environment.

Stability

The Stability, or strength (as measured by the Marshall test) achieved by various mix designs of cold-mix AMS is generally determined using either the Marshall or the Hveen method, the former being more compatible with field use, thus more commonly used. The overriding purpose of these methods is to evaluate the stability anticipated for the final asphaltic product and to document conformity with the various industry standards and specifications. In addition, if the end product is being used for load-bearing purposes, it is important to know whether it will maintain the required strength and stability to withstand repeated load applications (i.e., compression and flexural) without excess and permanent deformation and fatigue cracking, and whether the ultimate mix design will be sufficiently insensitive to moisture effects (Testa, 1997).

Mix designs play a major role in determining stability or strength in the final asphaltic product. Actual applications have ranged from a 95% contaminated soil with 5% emulsion, to 5% contaminated soil plus 90% class II 3/4-in. minus base rock and 5% emulsion. Essentially, one determines the end use or requirements and performance criteria and then designs the AMS mix to fit the use. As the equipment utilized to produce an asphaltic product is portable and certainly not complex, field test batches of 20 tons or more are utilized rather than bench-scale tests. In this manner the actual field mix is tested rather than a small hand-mixed batch.

Chemical Resistance

The testing and performance assessment of asphalt has traditionally focused on structural performance as pavement and building materials. However, when evaluating the long-term performance of asphalt liners produced with affected soil as part of the aggregate, the focus is on the chemical performance. Because of the great immiscibility of petroleum products with respect to the aqueous phases expected under impoundment conditions, large favorable free-energy change exists for preventing the release of contaminants from the asphalt. Therefore, the chemical behavior and performance of the petroleum contaminant should parallel the behavior and performance of the asphalt itself. Detailed chemical tests have been performed on asphalt liners for disposal sites of uranium mill tailings and for land disposal of radioactive waste. These studies can be used to make a preliminary evaluation of the use of affected soil for cold-mix AMS incorporation.

The resistance of asphalt to many reagents at atmospheric temperatures is well documented. Prolonged contact with dilute acidic solutions can result in hardening of the asphalt by the formation of asphaltenes. Nitric acid is very reactive with asphalt even in dilute solutions, whereas hydrochloric acid does not affect asphalt. Asphalt reaction with sulfuric acid is intermediate. Asphalt is generally more resistant to alkaline solutions than to acidic solutions, a favorable effect for asphalt liner. However, alkaline solutions can react to form salts such as sodium napthenates, whereas form excellent emulsifying agents. Theoretically, this could be a problem for affected soil if contaminants are mobilized in the emulsified solution. However, the emulsification depends on the degree of alkalinity and the diffusion and hydraulic resistances of the asphalt, which is generally extremely low: less than 10^{-12} and 10^{-9} cm/s, respectively. Without further experimental verification, emulsification of an asphalt liner is not expected to be important or leachable to the extent of releasing hydrocarbon constituents in excess of regulatory limits. The resistance of asphalt to selected chemicals under a variety of conditions has been described by the MRM Partnership (1988).

Aging

Of most importance to an asphalt liner, for example, is the effect of aging. Although not documented, hardening and other aging effects might increase mobilization of the petroleum contaminants from the AMS by supplying pathways out of the asphalt and by causing separation of petroleum constituents from the asphalt phases during aging. However, these effects would have to be excessive and affect a large proportion of the asphalt to mobilize the small amount of contaminants in the 10% fines of the aggregate.

Physical hardening due to peptization, paraffin crystallization, and volatilization occurs to different degrees in all types of asphalt and is unaffected by the presence of petroleum-contaminated soil as a small part of the aggregate. Chemical hardening, however, may be important. The rate of reaction of asphalt with oxygen is very temperature dependent and varies with asphalt type at high temperatures, but below 50°C the reactions are independent of temperature and asphalt type, are restricted to the asphalt surface, and should not be affected by affected soil. The hardening rate is higher in the presence of light, but

because of the dark conditions of the subsurface environment, only the aging reactions that occur in the dark are of importance to an asphalt liner. In the dark, oxygen is bound after short aging times as SO groups, and after long aging times as CO groups. Petroleum contaminants are not present in great enough quantities to affect the rate or degree of these reactions. Experiments show that the maximum depth of oxygen penetration is in the range 2.5 to 5 mm, but the rate of hardening decreases considerablly with time.

Biological Resistance

Microorganisms can degrade certain asphaltic components under ideal conditions. Research into microbial degradation of asphalt can be summarized as follows:

- No single microorganism will oxidize all asphaltic components.
- Microbial degradation occurs only at the outermost surfaces.
- The higher the molecular weight of an asphalt component, the more resistant it is to microbial degradation.
- Most soil asphalt-oxidizing microbes grow best at pH 6 to 8.
- Even under ideal conditions, microbial degradation rates do not exceed 10^{-6} cm/day (0.7 mm of penetration per 100 years) and are usually an order of magnitude less.
- The rate of anaerobic degradation is much slower than that of aerobic degradation.
- Microbial attack is fastest for stream-refined bitumens, followed by air-blown and, finally, coal-tar pitches.
- Microbial inhibitors are ineffective over long periods.
- Environmental factors (e.g., temperature, pH, state of hydrocarbons, nutrient and oxygen concentrations) have to be perfect for a very long time to result in any noticeable asphalt degradation.

Overall, microbial degradation will be important for all practical purposes.

Permeability

In considering the use of mine tailings and waste as an ingredient in producing an asphaltic liner, cap, or barrier, permeability is of course the primary consideration. Permeability tests were performed on a variety of liners after being subjected to aging tests. The permeabilities obtained for each liner are presented in Table 34.1. Permeability results generated on five representative samples of cold-mix AMS incorporating affected soil are presented in Table 34.2.

TABLE 34.1 Summary of Marshall Test Results for Stability

Sample No:	1	2	3	4	5	6
75:25 blend; class II base, $\frac{3}{4}$-in. and contaminated soil						
Asphalt in emulsion[a]	62–64	62–64	62–64	62–64	62–64	62–64
Residual asphalt in mixture[a,b]	5	5	5	6	6	6
Total mix water[a]	5.2	5.2	5.2	5.2	5.2	5.2
Compacted Specimen Data			Emulsion (%)			
Bulk density	2.08	2.07	2.11	2.05	2.07	2.05
Weight in air	1116.1	1125.1	1130.0	1120.1	1122.6	1120.7
Weight in water	584.4	586.5	599.0	577.2	584.4	577.5
Weight SSD	1120.1	1129.0	1134.1	1124.0	1126.5	1124.9
Thickness	$2\frac{5}{8}$ in.	$2\frac{11}{16}$ in.	$2\frac{5}{8}$ in.	$2\frac{11}{16}$ in.	$2\frac{11}{16}$ in.	$2\frac{11}{16}$ in.
Stability	3100	2350	2800	2450	2250	2200
Adjusted stability	2880	2090	2600	2180	2000	1960
Flow	30	27.5	31	31	30	24
Average stability	—	2520	—	—	2050	
Sample No:	7	8	9	10		
85:15 blend; class II base, $\frac{3}{4}$ in. and contaminated soil						
Residual asphalt in mixture[a,b]	6.5	6.5	6.5	6.5		
Bulk density	2.02	2.02	2.00	2.00		
Stability	3548	—	3260	—		
24-h soak	—	1410		1056		
Retained[a]	—	—	—	—	36.2	
Sample No:	11	12	13	14		
85:15 blend; class base, $\frac{3}{4}$ in. and contaminated soil						
Residual asphalt in mixture[a,b]	6	6	6	6		
Bulk density	2.01	2.03	2.01	2.03		
Stability	3158	—	2640			
24-h soak	—	1577	—	1201		
Retained[a]	—	—	—	—	47.9	
Moisture absorbed	×	×	×			
Maximum total voids[a]	—	—	—	×	×	×

[a]In percent.
[b]Emulsion.

TABLE 34.2 Anticipated Field Liner Permeabilities

Average Final Permeabilities (K, cm/s)	**Assumed Field Thickness (L, cm)**	**Effectiveness Factor (K/L, S^{-1})**
7×10^{-8}	10	7×10^{-9}
2×10^{-10}	0.12	2×10^{-9}
4×10^{-6}	0.8	5×10^{-6}
7×10^{-9}	0.9	8×10^{-9}
1×10^{-7}	10	8×10^{-8}
8×10^{-6}	10	8×10^{-7}
6×10^{-6}	10	6×10^{-7}
1×10^{-5}	10	1×10^{-6}

Accelerated aging tests of an asphalt liner at 20°C under oxygen partial pressures of 0.21, 1, and 1.7 atm, with continuous exposure as a liner at 20°C under varying oxygen partial pressures to an acidic leachate, have been performed. Solution pH, values of 2.5, 2.0, and 1.5 were designated as normal, intermediate, and highly accelerated conditions. Acidity levels were shown to have an unmeasurable effect on asphalt aging. Permeability was used as a means to measure the immediate effectiveness of the asphalt liner (Figure 34.4).

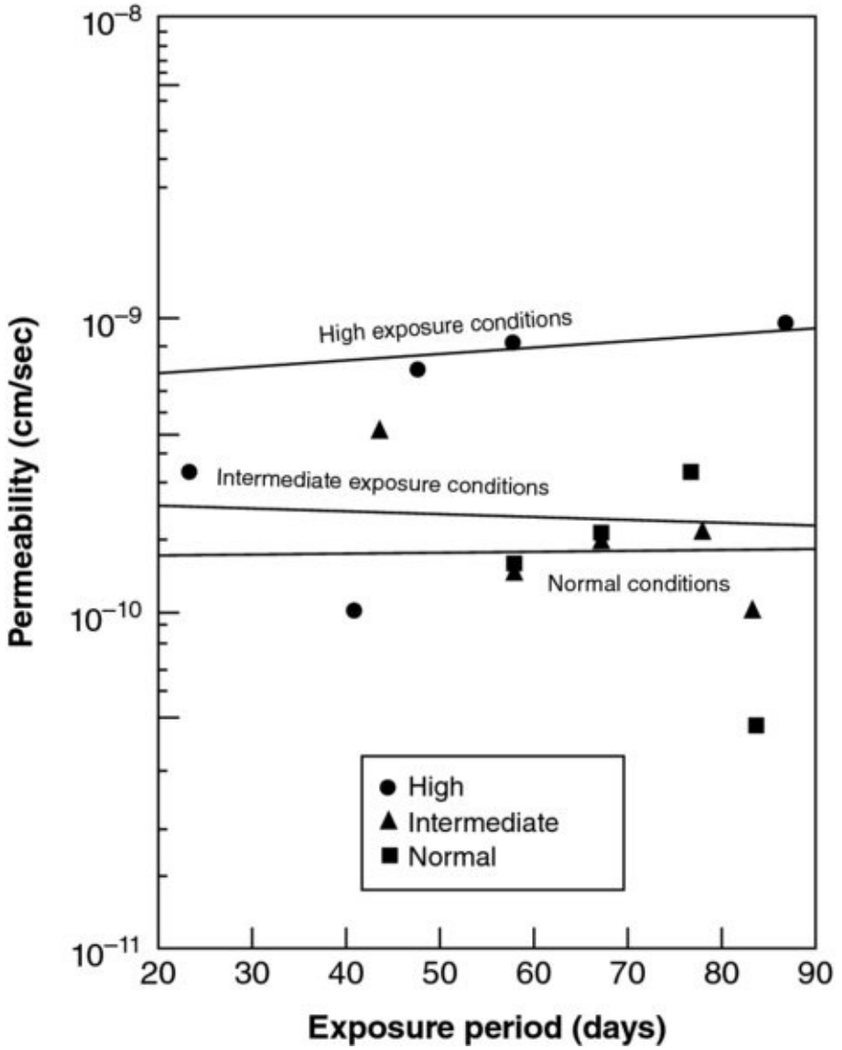

FIGURE 34.4 Permeability effects with exposure of an asphaltic liner.

Leachability

A normal asphaltic concrete or cold-mix AMS paving material is somewhat acceptable as an environmentally safe product even though there may be volatile organic compound emissions during manufacture and placement, notably in regard to the hot-mix process. The question of contamination is not frequently associated with asphaltic concrete even though certain halogenated volatile organics may be present in association with hot-mix bituminous products, notably those containing cut-back asphalt utilizing kerosene, diesel, or other solvents in their dilution process (Testa et al., 1992a,b).

Asphalt concrete or cold- mix AMS may be accepted by class III landfills and is commonly crushed and used as a component for road base material. The fact that there are few questions about the safety of asphaltic concrete is justified by the existence of thousands of miles of paved roadways constructed every year. Also, the performance of leachate tests on asphalt show a definite lack of contaminants that might leach out under extreme conditions. Leachate analytical results for certain petroleum constituents and other parameters in both hot- and cold-mix asphalt incorporating affected soil are presented in Table 34.3. Lead–zinc concentrations for preprocessed metals-affected soil and processed cold-mix asphalt via AMS are shown in Table 34.4. (see also Figure 34.5).

TABLE 34.3 Leachate Analysis of Typical Asphaltic Concrete Samples

Parameter	Analytical Method	Concentration	Unit	Detection Limit
Cold-mix asphalt				
Cyanide, total	SM412 E/D	ND[a]	mg/kg	1
Flash point	EPA 1010	>220	°F	5
pH	EPA 9045	7.62	±1	0.01
Sulfide	EPA 376.1	ND	mg/kg	1
Gasoline	EPA 8015	ND	mg/L	0.5
Diesel	EPA 418.1	ND	mg/L	0.5
Hot-mix asphalt				
Cyanide, total	SM412 E/D	ND	mg/kg	1
Flash point	EPA 1020	>220	°F	5
pH	EPA 9085	8.43	±1	0.01
Sulfide	EPA 376.1	ND	mg/kg	1
Gasoline	EPA 8015	ND	mg/L	0.5
Diesel	EPA 418.1	ND	mg/L	0.5

[a]ND, not detected above the respective detection limit.

TABLE 34.4 Results of Permeability Testing on Cold-Mix Asphalt

Asphalt Sample No.	Sample Length (cm)	Sample Diameter (cm)	Bulk Volume (cm^3)	Effective Permeability (mDa)	Hydraulic Conductivity (cm/s)
A-B-1	6.2	5.05	120.58	0.135	1.42×10^{-7}
A-B-2	6.81	5.06	136.94	0.013	1.37×10^{-8}
A-B-5	4.87	4.98	94.86	0.034	3.58×10^{-8}
A-B-7	6.42	5.06	129.10	0.096	1.01×10^{-7}
A-B-10	7.52	5.05	150.62	0.142	1.50×10^{-7}

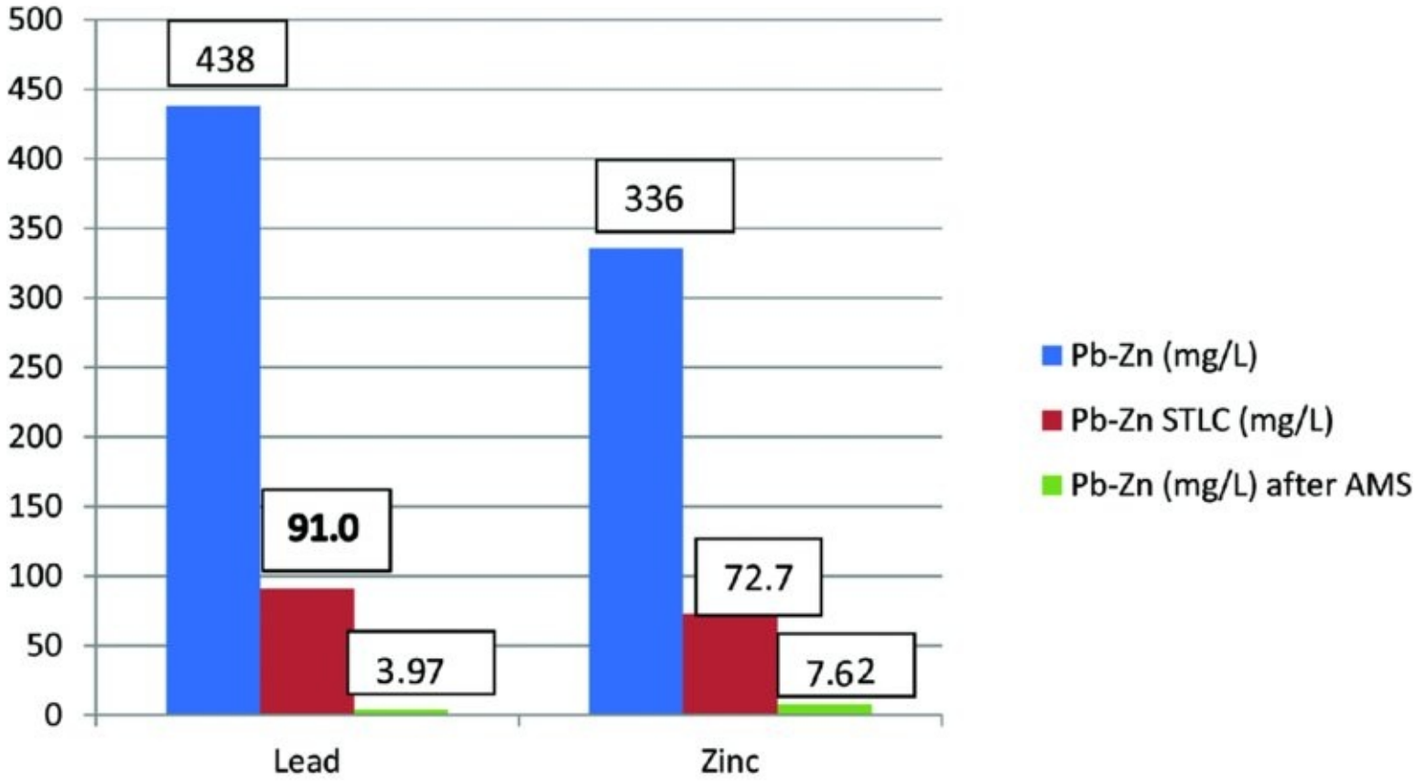

FIGURE 34.5 Analytical results for Pb–Zn prior to and after AMS.

Contaminant mobility, especially of metals, in the asphalted cement will be affected by many factors, including:

- Diffusivity and permeability of the asphalt cement as a whole (generally less than 10^{-12} and 10^{-9} cm/s, respectively)
- Solubility of species in the various aqueous, polar, and nonpolar phases
- Speciation of the contaminants: for example, UO_2 (nonmobile) versus $UO_2 \cdot nCO_3$ (highly mobile)
- Complexation with any chelating organics
- Redox reactions of metals across aqueous–organic phase boundaries
- Sorption on aggregate surfaces, along an asphalt–aqueous interface, or on colloids
- Precipitation of solid phases and/or colloids of metal sales, especially oxyhydroxide and carboxylic acid salts

Many of these properties are not known to the degree that specific contaminant release can be predicted. Leaching tests, the primary method of evaluating contaminant mobility in these systems, have been performed on a variety of asphalts. However, the low diffusivities and permeabilities of asphalt are obviously the greatest factor in the retention of contaminants in asphalt cements. Conditions that adversely affect the diffusivity and permeability will have the greatest adverse effect on contaminant mobility and release. The asphalt acts primarily as a physical containment to the contaminants and the aggregate. Of course, the physical properties of the asphalt cement result from the composition and structure of the asphalt.

Even though metals such as vanadium and nickel occur in asphalts at the hundreds of parts per million levels as well as many toxic organic components, asphalt leachates and products have never produced

toxic or contaminated solutions considered to be hazardous materials by the EPA. Asphalt's nonvolatile viscoelastic properties result in the general observation that asphalt leachates do not contain contaminant concentrations above the EPA's drinking water guidelines. Even in asphalts made with metal slags as an aggregate, metals do not become solubilized and do not leach from these asphalts in detectable concentrations even when used with strong acidic and alkaline solutions. Some typical test results for leaching of hot-mix asphalt are shown in Table 34.4 for several asphalts. Leaching test results for cold-mix asphalt are shown in Table 34.5.

TABLE 34.5 Summary of Leach Test Results from Seven Reclaimed Pavement Hot-Mix Asphalts Using U.S. EPA Test Procedures[a]

	Sample No.						
Parameter	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Barium (ppm)	<0.2	0.40	0.36	0.33	<0.2	<0.2	<2
Cadmium (ppm)	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.02
Chromium (ppm)	<0.05	0.52	<0.05	<0.05	<0.05	<0.05	0.10
Lead (ppm)	<0.2	1.80	<0.2	<0.2	<0.2	<0.2	<0.2
Silver (ppm)	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Arsenic (ppm)	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Selenium (ppm)	<0.025	<0.025	<0.025	<0.025	<0.025	<0.025	<0.005
Mercury (ppm)	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
1,4-Dichlorobenzene (ppb)	<50	<50	<50	<50	<50	<50	<12
2,4-Dinitrotoluene (ppb)	<50	<50	<50	<50	<50	<50	<12
Hexachlorobenzene (ppb)	<50	<50	<50	<50	<50	<50	<12
Hexachlorobutadiene (ppb)	<50	<50	<50	<50	<50	<50	<12
Hexachloroethane (ppb)	<50	<50	<50	<50	<50	<50	<12
Nitrobenzene (ppb)	<250	<250	<250	<250	<250	<250	<12
Pyridine (ppb)	<120	<120	<120	<120	<120	<120	<60
Cresylic acid (ppb)	<50	<50	<50	<50	<50	<50	<30
2-Methyl phenol (ppb)	<50	<50	<50	<50	<50	<50	<30
3-Methyl phenol (ppb)	<50	<50	<50	<50	<50	<50	<30
4-Methyl phenol (ppb)	<250	<250	<250	<250	<250	<250	<30
Pentachlorophenol (ppb)	<250	<250	<250	<250	<250	<250	<60
2,4,5-Trichlorophenol (ppb)	<50	<50	<50	<50	<50	<50	<30
2,4,6-Trichlorophenol (ppb)	<50	<50	<50	<50	<50	<50	<30
Naphthalene (ppb)	0.49	<0.13	<0.13	0.30	<0.13	<0.13	0.25
Acenaphthylene (ppb)	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.15
Acenaphthene (ppb)	0.14	<0.13	<0.13	<0.13	<0.13	<0.13	<0.194
Fluorene (ppb)	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.023

Phenantrene (ppb)	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.023
Anthracene (ppb)	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.015
Fluoranthene (ppb)	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.037
Pyrene (ppb)	<0.060	<0.060	<0.060	<0.060	<0.060	<0.060	<0.04
Benzo [*a*] anthracene (ppb)	<0.017	<0.017	<0.017	<0.017	<0.017	<0.017	<0.048
Chrysene (ppb)	<0.033	<0.033	<0.033	<0.033	<0.033	<0.033	<0.017
Benzo [*b*] fluoranthene (ppb)	<0.023	<0.023	<0.023	<0.023	<0.023	<0.023	<0.02
Benzo [*k*] fluoranthene (ppb)	<0.017	<0.017	<0.017	<0.017	0.050	<0.017	<0.022
Benzo [*a*] pyrene (ppb)	<0.024	<0.024	<0.024	<0.024	<0.024	<0.024	<0.023
Dibenzo [*a,h*] anthracene (ppb)	<0.068	<0.068	<0.068	<0.068	<0.068	<0.068	<0.018
Benzo [*g,h,i*] perylene (ppb)	<0.110	<0.110	<0.110	<0.110	<0.110	<0.110	<0.036
Indeno(1,2,3-*cd*)pyrene (ppb)	<0.022	<0.022	<0.022	<0.022	<0.022	<0.022	<0.021

Source: Modified after Kriech (1991) of the Heritage Research Group.

[a]Analytical tests include U.S. EPA Methods SW846-3350, 8080, 1311, 3510, 8310, and 3010.

Asphalt leachates that have contained detectable concentrations of contaminants have been obtained in studies of asphalted nuclear wastes (Amarantos and Petropoulos, 1982; Nikiforov et al., 1987; Daugherty et al., 1988; Fuhrmann et al., 1989). However, in all of these studies, high concentrations of salts were used, as high as 50% salt/50% asphalt. It is known that high salt concentrations in asphalt mixes disrupt the asphalt structure and will not occur in petroleum hydrocarbon–affected soils subjected to environmentally processed asphalt metho- dology.

On the other hand, in diffusion studies of radioactive wastes with normal salt contents, diffusion coefficients were measured to be as low as for normal asphalt conditions, with diffusion coefficients of 10^{-13} to 10^{-10} cm^2/s (R.J. Serne, personal communication). In all studies, researchers point out that experimental effects (e.g., slicing of thin asphalt membranes) may introduce errors that are not relevant to the field situation and tend to increase the diffusion coefficient observed.

A number of unplanned leaching experiments have been taking place with asphalt. Asphalt has been used for years to line domestic water reservoirs, especially in California, and to line fish-rearing ponds, with no adverse effects (E.D. Schlect, Asphalt Institute, personal communication). There are over 30 asphalt-lined fish-rearing ponds in Oregon and Washington. Trace metal and organic contamination is highly toxic to fry and developing fish, yet no adverse effects have been observed from the asphalt liners, indicating a high degree of chemical stability with respect to aqueous solutions and an absence of any toxicity effects.

Chemical Aspects

The chemical aspects associated with the incorporation of affected soil has been studied extensively in regard to pavement properties, leaching behavior, sensitivity to moisture damage, and function group analysis (Conca and Testa, 1992; Testa and Conca, 1992). These studies provide information that can be used to evaluate the stability of metals and other contaminants in soils that have been asphalted. These studies indicate that asphalted contaminated soil will be highly stable and will perform adequately as an end product. In general, the chemical structure, composition, and certain properties, such as leachability for cold- or hot-mix asphaltic end products, are similar. The greatest effects between the two types of preparation are on kinetically controlled reactions and sorption process. Asphalt, however, has a complex

and poorly understood chemistry and structure that depend on the crude petroleum source and whatever chemical treatment or modifiers might be added during processing. Asphalt has a large number of heteroatomic groups with a wide range of chemical reactivities, as shown in Figures 34.6 and 34.7.

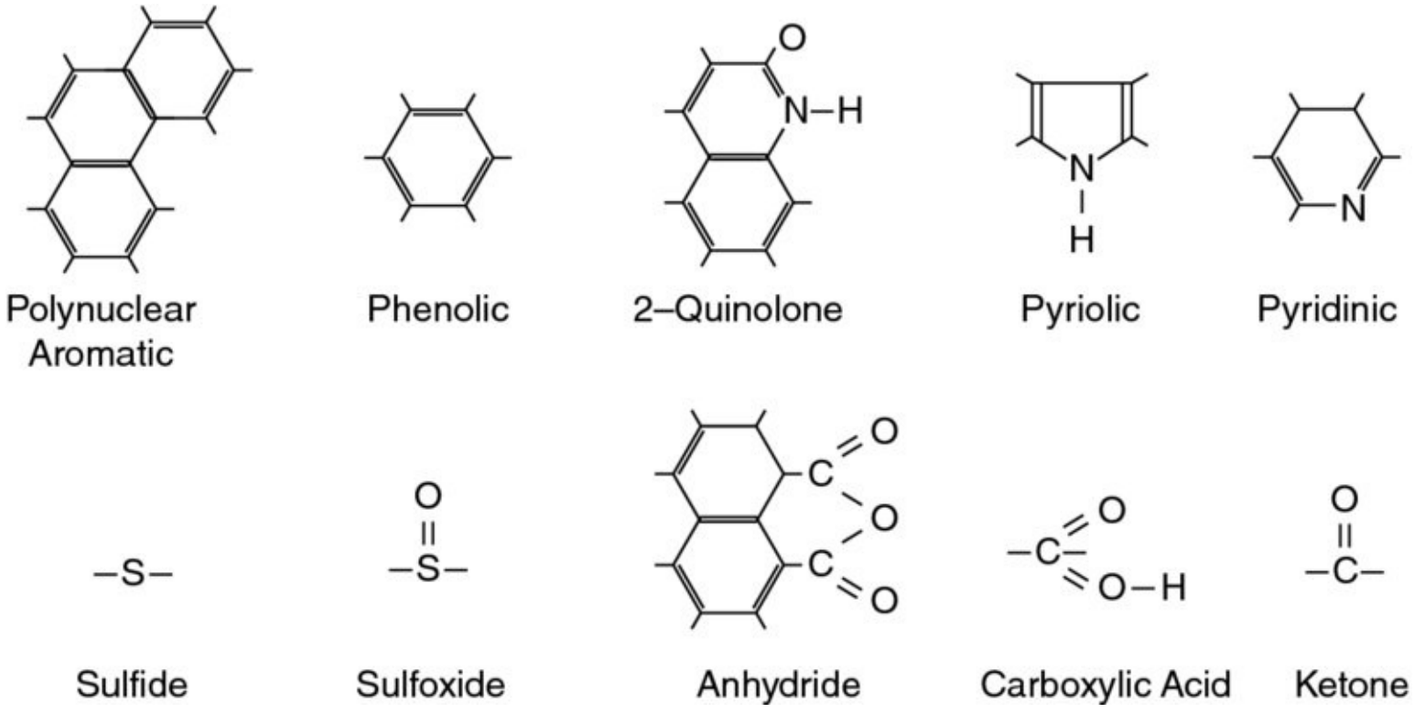

FIGURE 34.6 Important polar and nonpolar functional groups are present in asphalt. (From Testa and Conca, 1992.)

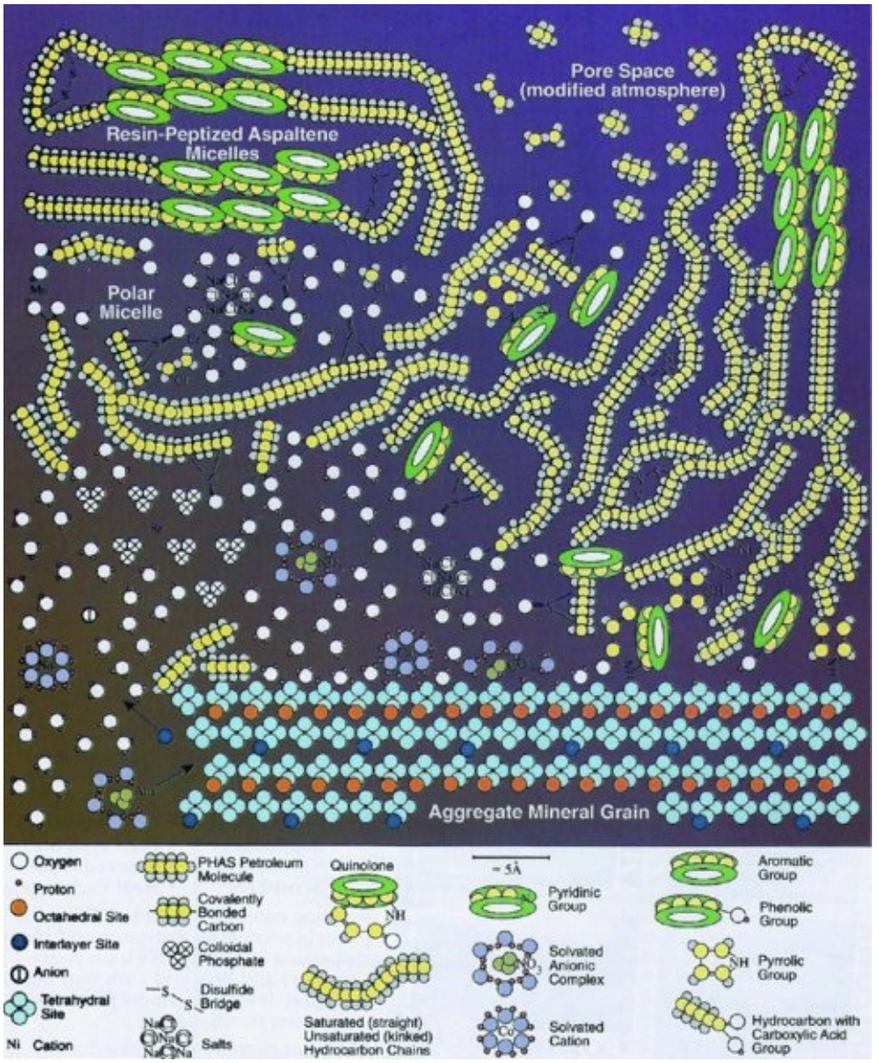

FIGURE 34.7 Schematic showing the asphalt–aggregate interface at the molecular level using space-filling and structural representations to illustrate important functional relationships. (From Conca and Testa, 1992.)

The overall number of distribution of these groups varies widely among different asphalts and much of their chemical behavior and performance. Functional relationships at the molecular level between the asphalt and aggregate interface were presented previously. For the best chemical performance, the asphalt should have high contents of pyridinic, phenolics, and ketone groups, which can be achieved by choosing the source material carefully. If the situation requires special stability or redundancy, small amounts of shale oil and lime can be used as additives. Situations and conditions that favor the presence of inorganic sulfur, monovalent salts, and high-ionic-strength solutions in the asphalt should be avoided because these conditions decrease the chemical stability of the asphalt cement by disruption of the functional group-aggregate bonds and by increasing the overall permeability. However, these conditions are not expected in the anticipated uses of asphalt cement to stabilize contaminants in metals-affected soil using environmentally processed remedial technology.

Discussion

AMS and associated processes can thus be described at best as user friendly. There currently exist a multitude of uses for cold-mix AMS incorporating affected soil. Constituents in the AMS process are encapsulated (according to 40 CFR definition) by asphalt emulsion (which becomes asphaltic cement

when compacted and cured); are fixated (per 40 CFR definition), as the asphaltic cement (which can be enhanced with polymerized asphalt emulsion) inhibits mobility, and are stabilized (according to 40 CFR definition) by being incorporated into a 95+% relative density compacted mass of extremely low permeability materials. Thus encapsulation, fixation, and stabilization present the rationale for the AMS effectiveness as an option to any conventional remedial process. By achieving encapsulation, fixation, and stabilization of constituents of concern utilizing asphaltic incorporation, a commercially successful end product is produced.

In consideration of certain factors, including durability, chemical resistance, aging, biological resistance, permeability, and leachability, cold-mix AMS is anticipated to perform more than adequately under normal conditions for a long period of time. Cold-mix asphalt will perform as well as, if not better than, hot-mix asphalt. The use of AMS as a liner, cap, or any number of other site-specific applications has vast potential. Hazardous waste cleanup projects become cold-mix asphalt production projects. Contaminated soil becomes a recoverable resource within the letter, spirit, and intent of current regulations.

Under California regulations, for example, non-RCRA-regulated recyclable materials used in a manner such that they are not considered to be “used in a manner constituting disposal” are not subject to the provisions of the health and safety codes of the state of California, Subsection 25143.2(b). Thus, if the recyclable materials satisfy the conditions of subsection 25143.2, they are (1) not considered hazardous waste, and (2) are conditionally exempt from hazardous waste regulations. Provided that the conditions summarized above are met, permanent fixation of contaminated soils via asphalt incorporation is a viable, cost-effective soil remediation option that can be accomplished within a relatively short period of time with minimal long-term liability. Furthermore, although highway-type paving materials as a resulting product is limited, multiple secondary markets exist.

Cementitious Processes

Mine tailings containing a wide variety of contaminants have been incorporated into a cementitious end product, and studies in the pursuit of this type of remediation strategy have increased over the past decade. Dealing with contaminants associated with acid rock drainage through stabilization methodologies via cementitious materials or as part of a process to produce a useful end product or recycled cementitious product has aroused interest in the research community over the past decade. The interest stems from the ongoing need to identify techniques that can control pH, reduce the mass transport of specific contaminants, and provide cohesiveness long-term in dealing with environmental concerns related to the management and remediation of mine tailings.

The overall concept is rather simple: that the cement is used as a binding agent and various mixtures of tailings are incorporated, along with other additives, depending on site-specific characteristics and availability of materials, to produce a workable end product or serve a beneficial use that is environmental by sound. The primary reason for this consideration not gaining much traction in the past probably reflects the lack of availability of cement-processing capabilities in the vicinity of where mine tailings or acid rock drainage occurs or has the potential to occur. This is changing, though. Canadian Electrolytic Zinc operates a zinc refinery on the north shore of the Beauhararnois Canal in Valleyfield, Quebec. The refinery produces a tailing slurry referred to as *jarosite* which until 1998 was deposited in ponds contained by clay dikes. The jarosite settles out and is characterized by low consistency and results in acidic pore water containing high metal concentrations. In 1998 the company implemented a new stabilization process, producing a chemically inert waste referred to as *jarofix*. Stabilization is achieved by washing and thickening at the plant site, followed by the addition of lime, cement, and water to the

thickened tailing paste to make jarofix. The jarofix is then hauled off site for disposal using a dry stacking technique which involves the placement of thin layers to allow for curing and solidification to a stiff consistency before other layers are deposited. In Indonesia in 2011 a company began planning construction of a new cement plant that would use copper tailings as a feedstock to produce a variety of cement products, including products for the purpose of infrastructure development. More mobile strategies have also been explored.

Stabilization Using Cementitious Materials

Cement production is accomplished by one of three processes: wet, dry, and dry with preheating or precalcining. In the production of cement, raw materials, including limestone, clay, and sand, are incorporated into the mix and are typically fed into a rotary kiln. Stabilization using cement involves a series of processes in which water contained in the waste reacts chemically with the cement to form hydrated calcium silicates and aluminate compounds; the solids act as an aggregate. The resulting cohesiveness provided by portland cement favorably limits the mobility of contaminants. In the case of arsenic, for example, the solidified cement limits the mobility of arsenic, while excess lime favorably traps arsenic as calcium arsenate in the absence of CO_2 (Picquet et al., 1995).

The overall performance of cementitious stabilization approaches is based on the intrinsic parameters of three main components: type and proportions of binder, tailings, and water. A ternary diagram showing chemical the compositional fields for portland cement and various additives is shown in Figure 34.8. In contrast to ordinary cement, the hardening process of cement–tailings mixtures reflects both hydration of the cement and the precipitation of hydrated phases from the pore water of the paste (Benzaazoua et al., 2002). The two-stage process begins with dissolution reactions, which is the primary anhydrous phase of cement. The second stage is characterized by precipitation reactions and direct hydration of the binder. This time-dependent set of reactions and dissolution and precipitation of the binder in the hardening process illustrates the importance of binders.

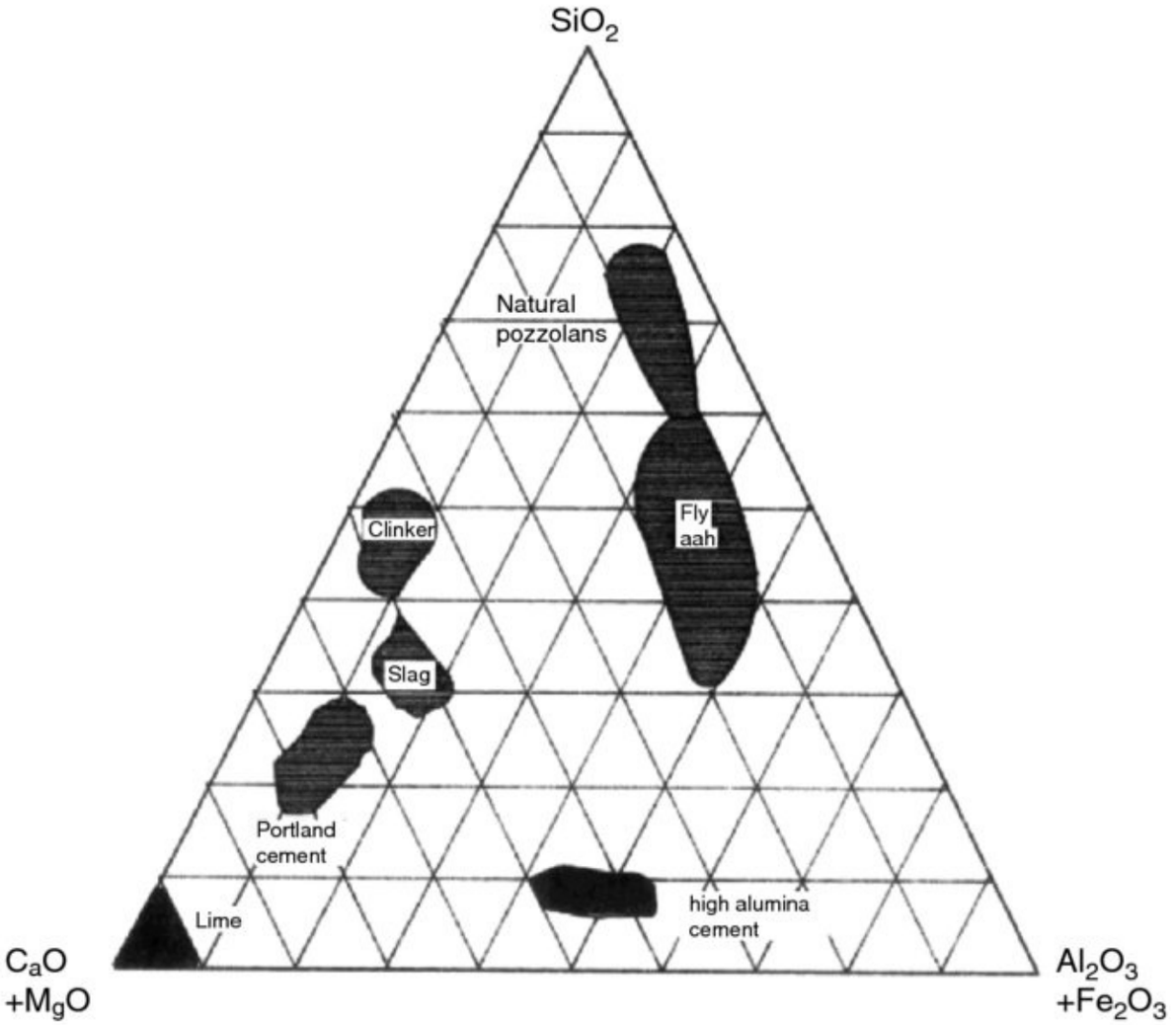

FIGURE 34.8 Ternary diagram showing chemical compositional fields for portland cement (types I and II cements), high alumna cement, clinker, fly ash, lime, natural pozzolons, and slag. (From Testa, 1992.)

The most common binder used in stabilizing contaminants is ordinary portland cement. To lower cost or improve final product performance, portland cement can be combined with fly ash, lime, slag, soluble silicates, clay, and cement kiln dust (Park, 2000; Poon et al., 1983). The use of other binder agents combined with portland cement consumes calcium hydroxide and alkalis during pozzolanic reactions, which contributes to the formation of secondary calcium silicate hydrates (CSH). CSH tends to fill voids and cause further reduction in capillary pore space and thus reduced leaching of contaminants. The general retardation of early-age strength gains with the use of pozzolanic and cementitious by-products; however, it is offset by considerable improvement in the long-term strength and impermeability of the end product (Jones, 1990).

Mine Tailings as an Additive to Portland Cement

Stabilization of sulfidic mine tailings using portland cement in combination with pozzolanic and cementitious materials has been shown to have merit (Nehdi and Tariq, 2007). A review of published literature on stabilization techniques of sulfidic mine tailings showed that variations of mine waste constituents and their interactions with different binding agents can hinder a stabilized system for a particular mine tailing composition under consideration (Table 34.6). Industrial by-products such as fly ash, slag and cement kiln dust can serve as a reinforcing agent in the stabilization of sulfidic mine tailings.

A blend of portland cement and cement kiln dust has been used as a stabilizing agent, in addition to natural oyster shells, to immobilize arsenic derived from mine tailings (Moon et al., 2010). Based on tailings retrieved from an Au–Ag mine in Korea, Kim and Jung (2011) reported that solidification using a 7 : 3 mixing ratio of tailings, and a 1 : 1 mixture of portland cement and blast furnace slag with 20% water content was one of the best methods studied for the remediation of arsenic and heavy metals (e.g., Cd, Cu, Pb, Zn), among other contaminated materials.

TABLE 34.6 Acid Mine Drainage Control Using Alkaline Additives

Contaminant	Material Stabilized	Stabilization Technique	Results	Reference
Sulfides	Sulfide-rich tailings from four Canadian mines; A1: containing ≈ 60% sulfides (essentially pyrite); A2: ≈ 40% sulfides; B: ≈ 30% sulfides; C: ≈ 10% sulfides.	OPC type I and sulfate-resistant cement type V; fly ash, and blast furnace slag. Mixing water types (lake water, municipal water, and sulfate-rich process water). Paste backfill preparation using binders and sulfidic tailings.	OPC and fly ash binders proved suitable for high-sulfide tailings, producing adequate strength after 28, 56, and 91 days of curing time. Slag-based binders exhibited hydration inhibition until after 120 days of curing time and were found appropriate only for medium- and low-sulfur-rich tailings.	Benzaazoua et al. (2002)
	Sulfidic mine tailings from milled gold ore containing 60% sulfide content. Fine-grained tailings containing pyrite and arsenopyrite in about equal amounts.	OPC, aluminous cement, ground blast furnace slag cement. Paste backfill preparation by mixing hydraulic binders with sulfidic tailings.	Leaching experiments were done using a shaked flask and soxhlet extractor. The ability of stabilized samples to retain arsenic was checked after 500 days of conditioning. The main factor in fixing arsenic was the calcium content of the binding agent. Cemented stabilized matrix rich in $Ca(OH)_2$ maintained a neutral-to-alkaline environment with pH conditions and calcium activity favorable for the inhibition of arsenopyrite oxidation.	Benzaazoua et al. (2004)
Copper, sulfur, zinc, sulfides, sulfates	Zinc and copper sulfide ores with total sulfur (S) and sulfate (SO_4^{2-}) contents of 96.3 and 18.9	Calcite ($CaCO_3$) and quicklime (CaO) addition to the tailings.	Calcite was found preferable to quicklime for maintaining long-term neutral pH conditions in the tailings treated. With the exception of zinc, acceptable levels of dissolved metal concentrations were achieved with calcite-treated tailings.	Catalan and Yin (2003)

	mg S/g of tailings, respectively. The sulfide content estimated to be 77.4 mg S/g tailings.			
Lead, zinc	Contaminated soil from tailings pond of lead and zinc mine, containing Zn (3366 ppm), Pb (12245 ppm), Cu (444 ppm), and Cd (25 ppm).	Addition of fly ash containing 90.40% ash, 7.09% fixed carbon, 2.50% volatile matter, and red mud from metallurgical treatment of bauxite ores.	The addition of 15% fly ash and a mixture of 7.5% fly ash and 7.5% red mud by mass to contaminated soil drastically reduced the heavy metal contents of the soil leachates.	Ciccu et al. (2003)
Copper, iron, lead, sulfur, zinc	Reactive tailings rich in Fe, S, Cu, Pb, and Zn.	Cement kiln dust (CKD), red mud bauxite (RMB).	10% CKD and 10% mixture of CKD and RMB allowed neutral pH over 365 days of batch leaching tests.	Doye and Duchesne (2003)
Copper, gold, silver, zinc	Mine tailings from copper, zinc, silver, and gold.	Cement kiln dust addition (10% by weight) using layered commingling technique.	The compacted layers containing CKD acted as a trap for different metals favoring precipitation in addition to the alkaline reservoir to neutralize acidity and reduction in bacterial activity.	Fortin et al. (2000)
Copper, lead, nickel	Mine soils containing Cu, Ni, and Pb, etc.	CaO and Na_2 S addition to soils containing heavy metals.	Quicklime and sodium sulfide had good immobilization efficiencies for Cu, Ni, and Pb.	Jang et al. (1998)
Iron, sulfur	Sample 1: fine-grained reactive mine tailings containing 4.33% iron and 8.5% sulfur. Sample 2: tailings with comparatively lower fineness	Agglomerates preparation using OPC and fly ash with tailings. Fly ash: 5 to 20% by mass, and OPC: 2.5%, 5%, 7.5%, and 10%.	Tests on tailings agglomerates prepared using fly ash and OPC resulted in much lower level of extractable ions concentration and well below the regulatory level than from agglomerates prepared using either fly ash or cement alone. Agglomeration of reactive tailings required 10% cement by mass, and addition of 20% fly ash was found to be equivalent to 5% cement in terms of leaching control.	Misra et al. (1996)

	and having 3.0% sulfur.			
Aluminum, iron, magnesium, sulfates	High-sulfate content mine tailings: Al_2O_3 (6.6%), Fe_2O_3 (41.07%), MgO (1.31%).	Lime, fly ash (class C) and aluminum (110 ppm) were used as additives to mine tailings.	5% lime and 10% type C fly ash in combination with 110 ppm aluminum resulted in formation of a solid monolith capable of producing more than 1 MPa of unconfined compression strength and reduction in hydraulic conductivity to 1.96×10^{-6} cm/s.	Mohamed et al. (2002)
Sulfides	Sulfidic tailings containing 27% sulfur.	Lignite fly ash (class C), amount ranging from 10 to 63% by weight.	Fly ash addition at a lower amount (10%) increased the pH of leachates to values of 8.6 to 10 and decreased dissolved concentrations of contaminants, mainly Zn and Mn. Higher fly ash addition (31 and 63% w/w) reduced water permeability of the material from 1.2×10^{-5} cm/s to 3×10^{-7} and 2.5×10^{-8} cm/s, respectively. Long-term (600 days) laboratory column kinetic tests were performed.	Xenedis et al. (2002)
Chromium, copper, lead, zinc	Metal-enriched gold-mining residue (Cr, Cu, Pb, Zn).	OPC mixture with tailings.	10 to 20% addition of OPC, unconfined compressive strength values were 1.1 to 3.3 MPa and hydraulic conductivities were in the range of 1.04×10^{-9} to 2.1×10^{-9} m/s. Metal retaining efficiencies were greater than 87%.	Yilmaz et al. (2003)
Copper, iron, lead, sulfur	Soil contaminated with heavy metals Pb (153 mg/kg), Cu (510 mg/kg), Fe (15.3%), S (14.63%) from an old mining and smelting area.	Lime and OPC. Lime/soil and cement/soil mixtures at ratios of 1:15, 1:20, and 1:25 by mass.	The addition of lime and cement to contaminated soil containing Cu, Pb, and Fe reduced the leachability of the contaminated metals. Additive/soil ratio of 1:15 was found superior for both lime and cement, giving rise to a solubility reduction of Cu, Fe, and Pb. Cu: Additive/soil mixture = 1:15; TCLP solubility decreased by 94% for a lime/soil mixture and 48% for a cement/soil mixture, respectively. FE: Additive/soil mixture = 1:15; TCLP solubility decreased by 90% for a lime/soil mixture and 71% for a cement/soil mixture, respectively. Pb: Solubility found below the regulatory limit of 5 mg/L.	Yukselen and Alpasalan (2001)

Source: Modified after Nehdi and Tariq (2007).

Celik et al. (htpp://wmr.sagepub.com/content/24/3/215. abstract) studied the feasibility of utilizing tailings as an additive material in portland cement production and investigated the effects of the tailings on the compressive strength properties of portland cement. Chemical and physical properties,

mineralogical composition, particle size distribution, and the microstructure of the tailings were determined by Fourier transform infrared spectroscopy, x-ray diffractometry, particle size analysis (e.g., using a Mastersizer), and scanning electron microscopy. Cement mortars were prepared by intergrinding portland cement with dried tailings. The composition of the cement clinkers was adjusted to contain 5, 15, and 25% wt/wt dried tailings, and silica fume and fly ash samples (C and F types) were added to the clinker in varying ratios. Various amounts of tailings, silica fume, fly ashes, and admixtures were tested for compressive strength values after 2, 7, 28, and 56 days according to the European Standard (EN 196-1). The results indicated that gold tailings up to 25% in clinker could be used beneficially as an additive in portland cement production, and that the gold tailings used in the cement, and blended with silica fume and type C fly ash, resulted in higher compressive strength values. The annual output of desulfurized and skimming tailings is on the order of 220,000 tons at the old Ansteel base and 100,000 tons annually at the new base. Incorporation of slag and tailings up to 30 wt% was found to be acceptable while maintaining acceptable compressive strength and rupture strength (Han et al., 2011).

Nathwani and Phillips (1978) have investigated the leacheability of ^{226}Ra from soil at a uranium refinery located at Port Hope, Ontario, and recently, Nathwani and Phillips (1980) reported that the fraction of ^{226}Ra leached from uranium mill tailings could be reduced by one or two orders of magnitude by solidifying mill tailings with cement or an admixture of cement and peat or clay. The most effective consolidation mixture reported was a 70 : 30 tailings to consolidating mixture comprised of cement, peat, and clay in the ratio 50 : 30 : 20.

Mine Tailings as Backfill

Another interest and innovative approach is the use of cement as a binder for tailings, which are then pumped as a slurry underground to fill voids and support underground workings (http://www.tailings.info/backfill.htm). Materials for the backfilling of underground workings have included cement fill, paste or slurry fill, hydraulic sand fill, and dry rock fill. Backfilling of underground workings, as at the Cleveland potash, location and the Boulby mine in the UK using a cement binder has proved beneficial for the removal of in situ pillars containing ore material while maintaining support and preventing head collapse and subsidence. The potential for rock bursts is also minimized and the binder can help minimize groundwater contamination. However, costs may be prohibitive since a cementitious binder is required and the tailings typically would need to be dewatered. Also, care must be taken to avoid plugging and formation of rat holes and liquefaction of the backfill material.

Other Manufacturing Processes

Use of various manufacturing processes, such as brick or tile manufacturing, has merit, but as with cement production, the availability of a processing plant in relatively close proximity to an area where acid rock drainage is occurring or is likely to occur is problematic. However, from a process and resource recovery perspective, such processes continue to be evaluated. Contaminated soil, mine tailings, and other materials have been used to produce commodities such as bricks and tiles. The materials or tailings are used essentially to replace one or a combination of raw materials, such as the firing clay or shale. Brick manufacturing incorporates the blending of shale and clay into a plasticized mixture, which is then extruded and molded into its final form. When dried, the brick or tile is fired in a kiln, where temperatures reach approximately 2000°F. The brick is fired for approximately 12 h, which allows inorganics to be incorporated into the vitrified brick end product. Brick manufacturing facilities that incorporate contaminated materials are known to exist in California, North Carolina, Ohio, South

Carolina and Virginia.

Mine Tailings as an additive in Bricks and Tiles

Producing bricks from mill tailings has been examined by Adhikari (2007) in the Kolas gold fields in Karnataka. The plasticity index of zero required that the additives provide some bounding capability: portland cement in addition to what was described as black cotton soils and red soils. Each additive was mixed separately with the mill tailings in different proportions by weight, and a large number of bricks were prepared using metallic molds. The bricks were termed cement-tailings or soil-tailings bricks, depending on the additives used. Following curing for different periods, their corresponding compressive strengths were determined. Bricks with 20% cement and 14 days of curing were found to be suitable. The soil-tailings bricks were sun-dried and then fired in a furnace at various temperatures. The quality of bricks was assessed in terms of linear shrinkage, water absorption, and compressive strength. The cost analysis revealed that cement-tailings bricks would be uneconomical, whereas the soil-tailings bricks would be very economical. Brick manufacturing is needed in many areas, and Figure 34.9 illustrates a plant in the city of Lake Elsinore, California.

FIGURE 34.9 Brick manufacturing from an aggregate and clay mine located in the Lake Elsinore, California. Depending on the clay strata mined and clay type, several varieties of colored bricks are produced for a variety of uses (Courtesy of S. M. Testa.)

The Idaho–Maryland Mining Corporation is in the process of permitting reopening of the historic Idaho–

Maryland mine in Grass Valley, California. The Idaho–maryland mine was the second-largest underground gold mine in California, producing about 2.4 million ounces of gold from 1861 until 1956. Part of the owners' proposal is to incorporate mine tailings to product tiles. The potential for the use of mine tailings materials for tile manufacturing has recently been evaluated. Economic considerations are whether this reuse recovery option can be implemented successfully at a scale commensurate with the quantity of tile projected to be manufactured; and whether marketing efforts for the quantity of tile could be produced at a price that is cost-effective in lieu of production costs.

Pigments

Innovative resource recovery solutions to dealing with acid mine drainage, albeit on a small scale, are being explored. Natural iron oxides are mined at about a dozen sites in the United States and worldwide. Limited by the price of competitively mined products, Potter (2000) estimates the commercial value of this product to be on the order of $100 to $400 per ton. Iron oxide sludge recovered from a channel at an abandoned coal mine in southwestern Pennsylvania was processed and used as a raw material in pigment production (Hedin, 2003). The channel carried mine discharge at a rate of 9500 m^3/day, with a pH of 6.2, an Fe concentration of 72 mg/L, and an alkalinity of 312 mg/L as $CaCO_3$. A total of 1000 tons of iron oxide sludge was used to produce a burnt sienna pigment that is used in a variety of coloring applications. This product would normally have to be imported from other U.S. sources and from Mediterranean and Asian countries.

References and Suggested Reading

Adhikari, R.S., 2007. Use of gold mill tailings in making bricks: a feasibility study: Waste Management Resources, vol. 25, no. 5, pp. 475–482.

Amarantos, S.G., and Petropoulos, J.H., 1981. Certain Aspects of Leaching Kinetics of Solidified Radioactive Wastes: Laboratory Studies. DEMO 81/2. Greek Atomic Energy Commission, Athens, Greece.

Asphalt Institute, 1979. A Basic Asphalt Emulsion Manual. Manual Series 19. Asphalt Institute, College Park, MD.

Asphalt Institute, 1982. Principles of Construction of Hot-Mix Asphalt Pavements. Manual Series 22. Asphalt Institute, College Park, MD.

Asphalt Institute, 1983. Asphalt Cold-Mix Recycling. Manual Series 21. Asphalt Institute, College Park, MD.

Atlas, R.M., 1981. Microbial degradation of petroleum hydrocarbons and environmental perspective. Microbiological Reviews, pp. 180–209.

Benedetto, A.T., Lottman, L.P., Cratin, P.D. and Ensley, E.K., 1980. Asphalt Adhesion and Interfacial Phenomena. Highway Research Record No. 340, National Research Council, Highway Research Board, Washington, DC.

Benzaazoua, M., Belem, T., and Bussiere, B., 2002. Chemical factors that influence the performance of mine sulphidic paste backfill: Chemical Concrete Research, vol. 32, pp. 1133–1144.

Benzaazoua, M., Fall, M. and Belem, T., 2004. A contribution to understanding the hardening process of

cemented paste. Mineralogical Engineering, vol. 17, pp. 141–153.

Buelt, J.L., 1983. Liner Evaluation for Uranium Mill Tailings. Final Report, PHL-4842. Pacific Northwest Laboratory, Richland, WA.

Catalan, L.J.J., and Yin, G., 2003. Comparison of calcite to quick-lime for amending partially oxidized sulphidic mine tailings before flooding. Environmental Science and Technology, vol. 37, pp. 1408–1413.

Celik, O., Elbeyli, I.Y., and Piskin, S., Utilization of gold tailings as an additive in portland cement. Waste Management Resources, SAGA Online Journal. htpp://wmr.sagepub.com/ content/24/3/215.abstract.

Ciccu, R., Ghiani, M., Serci, A., Fadda, S., Peretti, R., and Zucca, A., 2003. Heavy metal immobilization in the mining-contaminated soils using various industrial wastes. Mineralogical Engineering, vol. 16, pp. 187–192.

Conca, J.L., and Testa, S.M., 1992. Chemical aspects of environmentally processed asphalt. In: Proceedings of the International Symposium on Asphaltene Particles in Fossil Fuel Exploration, Recovery, Refining and Production Process, Las Vegas, NV.

Daiev, C.T., and Vassilev, G.P., 1985. On the diffusion of ^{90}Sr from radioactive waste bituminized by the mould method. Journal of Nuclear Materials, vol. 127, pp. 132–136.

Daugherty, D.R., Pietrzak, R.F., Fuhrmann, M., and Columbo, P., 1988. An Experimental Survey of the Factors That Affect Leaching from Low-Level Radioactive Waste Forms. BNL-52125. Brookhaven National Laboratory, Upton, NY.

Doyle, I., and Duchesne, J., 2003. Neutralization of acid mine drainage with alkaline industrial residues: laboratory investigation using batch-leaching tests. Applied Geochemistry, vol. 18, pp. 1197–1213.

Eschrich, H., 1980. Properties and Long-Term Behavior of Bitumen and Radioactive Waste–Bitumen Mixtures. SKBF KBS Technical Report 80-14. Swedish Nuclear Fuel and Waste Management Company, Stockholm, Sweden

Fortin, S., Lamontagne, A., and Poulin, R., 2000. The Use of Basic Additives to Tailings in Layered Co-mingling to Improve AMD Control. InfoMine, Inc., Vancouver, BC, Canada.

Fuhrmann, M., Pietrzak, R.F., Franz, E.M., Heiser, J.H., III, and Columbo, P., 1989. Optimization of the Factors That Accelerate Leaching. BNL-52204. Brookhaven National Laboratory, Upton, NY.

Han, Y.X., Li, L.X., Liu, X., Song, N.B., and Wang, Y.B., 2011. Cementing property of cement with desulfurization and skimming slag tailings powder. Advances in Materials Research, vol. 158, pp. 18–24.

Harris, J.O., 1958. Preliminary studies on the effect of micro-organisms on the physical properties of asphalt. Transactions of the Kansas Academy of Science, vol. 61, pp. 110–113.

Haxo, H.E., Jr., 1976. Assessing Synthetic and Admixed Materials for Liner Landfills, Inc. Gas and Leachate from Landfills, Formation, Collection and Treatment, E.J. Genetelli and J. Circello, eds. EPA 600/9-76-004, MTIS Report PB251161, U.S. EPA, Cincinnati, OH, pp. 130–158.

Hedin, R.S., 2003. Recovery of marketable iron oxide from mine drainage in the USA. Land Contamination and Remediation, vol. 11, no. 2, pp. 93–97.

Hickle, R.D., 1976. Impermeable asphalt concrete pond liner. Civil Engineering, pp. 56–59.

Jang, A., Choi, Y.S., and Kim, S., 1998. Batch and column tests for the development of an immobilization technology for toxic heavy metals in contaminated soils of closed mine. Water Science Technology, vol. 37, pp. 81–88.

Jiang, W., and Roy, D.M., 1995. Microstructural aspects of high performance cement-based materials. Material Research Society Symposium Proceedings, vol. 370, pp. 115–124.

Jones, L.W., 1990. Interference mechanisms in waste stabilization/solidification processes. Journal of Hazardous Materials, vol. 24, pp. 83–88.

Jones, T.K., 1965. Effects of bacteria and fungi on asphalt. Material Protection, vol. 4, p. 39.

Kandhal, P.S., 1993. Waste materials in hot mix asphalt: an overview. In: Waste Materials in Hot Mix Asphalt, H.F. Waller, ed. ASTM, International, West Conshohocken, PA, pp. 3–36.

Kim, J.W., and Jung, M.C., 2011. Solidification of arsenic and heavy metal containing tailings using cement and blast furnace slag. Environmental Geochemical Health, vol. 33, Supplement, pp. 151–158.

Kriech, A.J., 1990. Evaluation of Hot Mix Asphalt for Leachability. HRG #3959AOM3. Heritage Research Group, Indianapolis, IN.

Misra, M., Yang, K., and Mehta, R.K., 1996. Application of fly ash in the agglomeration of reactive mine tailings. Journal of Hazardous Materials, vol. 51, pp. 181–192.

Mohamed, A.M.O., Hossein, M., and Hassani, F.P., 2002. Hydro-mechanical evaluation of stabilized mine tailings. Environmental Geology, vol. 41, pp. 749–759.

Moon, D.H., Kim, K.-W., Yoon, I.-H., Grubb, D.G., Shin, D.T., Cheong, K.H., Choi, H.-I., Ok, Y.S, and Park, J.H., 2010. Stabilization of arsenic-contaminated mine tailings using natural and calcined oyster shells. Environmental Earth Sciences, vol. 61, no. 6, pp. 1301–1308.

MRM Partnership, 1988. Bituminous and Asphaltic Membranes for Radioactive Waste Repositories on Land. Report to the Department of Environment, DOE/RW/87.009. MRM, Bristol, UK.

Nathwani, J.S., and Phillips, C.R., 1978. Leachability of Ra-226 from uranium mill tailings consolidated with naturally occurring materials and/or cement. Water, Air, and Soil Pollution. vol. 14, no. 1, pp. 379–387.

Nathwani, J.S., and Phillips, C.R., 1980. Leachability of Ra-226 from uranium mill tailings consolidated with naturally occurring materials and/or cement: Water, Air, and Soil Pollution, vol. 14, no. 1, pp. 379–387.

Nehdi, M., and Tariq, A., 2007. Stabilization of sulphidic mine tailings for prevention of metal release and acid drainage using cementitious materials: a review. Journal of Environmental Engineering and Science, vol. 6, pp. 423–436.

Nikiforov, A.S., Zakharova, K.P., and Polyakov, A.S., 1987. Physicochemical foundations of bituminization of liquid radioactive wastes from a nuclear power plant with RBMK reactor and the properties of the compounds formed. Soviet Atomic Energy, Vol. 61, pp. 664–668.

Park, C.K., 2000. Hydration and solidification of hazardous wastes containing heavy metals using modified cementitious materials. Cement and Concrete Research, vol. 30, pp. 429–435.

Picquet, I., Benzaazoua, M., Marion, P., and Videau, G., 1995. Inertage de steriles miniers arseno-sulfures dans des liants hydrauliques. In: Congres International PSS Dechets, Nancy France, J.M. Cases and F. Thomas, eds., vol. 20, pp. 941– 947.

Poon, C.S., Peter, C.J., and Perry, R., 1983. Use of stabilization processes in the control of toxic wastes. Effluent Water Treatment Journal, vol. 23, pp. 451–459.

Potter, M.J., 2000. Iron oxide pigments, 2000 annual review. In: U.S. Geological Survey Mineral Yearbook, 1999. U.S. Department of the Interior, Washington, DC.

Preston, R.L., and Testa, S.M., 1991. Permanent fixation of petroleum-contaminated soils. In: Proceedings of the National Research and Development Conference on the Control of Hazardous Materials, Anaheim, CA, pp. 4–10.

Testa, S.M., 1997. The Reuse and Recycling of Contaminated Soil. CRC Press/Lewis Publishers, Boca Raton, FL, 268 pp.

Testa, S.M., and Conca, J.L., 1992. When contaminated soil meets the road. Soils, pp. 32–38.

Testa, S.M., and Patton, D.L., 1992a. Paving market shows promise. Soils, pp. 9–11.

Testab, S.M., and Patton, D.L., 1992. Add zinc and lead to pavement recipe., Soils, pp. 22–35.

Testa, S.M., Patton, D.L., and Conca, J.L., 1992a. The use of environmentally processed asphalt as a contaminated soils remediation method. In: Proceedings of the Hazardous Materials Control Research Institute Conference, Hazardous Materials Control South, New Orleans.

Testa, S.M., Patton, D.L., and Conca, J.L., 1992b. The use of environmentally processed asphalt as a contaminated soils remediation method. In Petroleum Contaminated Soils E.J. Clarence, and P.T., Kostecki, eds. CRC Press/Lewis Publishers, Boca Raton, FL, vol. 4.

Testa, S.M., Patton, D.L., and Conca, J.L., 1992c. Fixation of petroleum contaminated soils via cold-mix asphalt for use as a liner. In: Proceedings of the Hazardous Materials Control Research Institute, Hagardous Materials Control South, New Orleans, LA.

U.S. Environmental Protection Agency, 1991. Treatment of Lead-Contaminated Soil. USEPA Superfund Engineering Issue. EPA 540/2-91-009. U.S. EPA, Washington, DC.

Wolfe, D.L., Armentrout, D., Arends, C.B., Baker, H.M., Plancher, H., and Petersen, C.J., 1986. Crude Source Effects of the Chemical Morphological, and Viscoelastic Properties of Styrene/ Butadiene Latex Modified Asphalt Cements, Transportation Research Record 1096. Transportation Research, Board, National Research Council, Washington, DC, pp. 12–21.

Xenidis, A., Mylona, E., and Paspaliaris, I., 2002. Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. Waste Management, vol. 22, pp. 631–641.

Yilmaz, O., Unlu, K., and Cokca, E., 2003. Solidification/stabilization of hazardous wastes containing metals and organic contaminants. Journal of Environmental Engineering, vol. 129, pp. 366–376.

Yukselen, M.A., and Alpasalan, B., 2001. Case study-leaching of metals from soil contaminated by mining activities. Journal of Hazardous Materials, vol. B87, pp. 289–300.

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Case Studies for Acid Mine Drainage

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Resource recovery and recycling are important aspects of sustainable business and long-term planning. Recycling includes the land resources, and redevelopment of former or abandoned mine sites is an appropriate way to revitalize the environment and improve communities. These case studies, primarily from U.S. Environmental Protection Agency (EPA) files, include several former mine sites where the challenges of ecological revitalization and land recycling have been met successfully. Other acid mine drainage case studies are available through the Interstate Technology and Regulatory Council (IRTRC) (2006, 2011). Over two dozen remediation technologies for different media are highlighted in Table 35.1, with a description of the methods based on extensive research by the ITRC (2011).

Table 35.1 Summary of Various Acid Drainage Technologies, Media, and Noted Examples

Technology	Media[a]	Noted Examples
Administrative and engineering controls	MIW and MSW	Abandoned Tennessee Valley Authority site, AL Annapolis lead mine, MO Tar Creek Superfund site, OK Black Butte mercury mine, OR Commerce/Mayer Ranch, OK Copper basin mine, TN Ely copper mine, VT Horse Heaven mine, OR Ore Hill mine, NH Kerramerican mine, ME Southeastern Ohio coal mine Gribbons Basin site, MT Kennecott south zone, VT Leviathan mine, CA Orono–Dunweg site, MO
Aeration treatment systems	MIW	Leviathan mines, CA
Anoxic limestone drains	MIW	Ohio abandoned bituminous coals, southeastern, OH Copper basin mining site, TN Hartshorne/Whitlock-Jones, OK Valzinco mine, VA Tecumseh AML Site 262, IN Tennessee Valley Authority, AL
Backfilling and subaqueous disposal	MIW and MSW	Hume mine, MO Cottonwood Creek mine, MO Valzinco mine, VA Copper basin, TN

		Tar Creek Superfund site, OK McNeely green reclamation, OK Bark Camp, PA Central City/Clear Creek Superfund site, CO
Biochemical reactors	MIW	Leviathan mine, CA Golinsky mine, CA Stowell mine, CA Copper basin, TN Central City/Clear Creek Superfund site, CO Alpine County, CA, 1 and 2
Capping, covers and grading	MSW	Annapolis lead mine, MO Big River mine site, MO Dunka mine, MN Gribbons basin, MT Horse heaven, OR Iron Mountain mine, CA Kerramerican, ME Magmont mine site, MO Orono–Dunweg, MO Valzinco mine, VA Copper basin, TN Bark Camp, PA Cottonwood Creek, MO Ely copper mine, VT Hume mine, MO I-99 remediation, PA Lava Cap mine, NV Numerous coal mine sites, OH McNeely green, OK Stull yard, ID Tecumseh, AM Site 262, IN
Chemical precipitation	MIW	Multiple Ohio sites Copper basin mining, TN I-99 remediation, PA Iron Mountain mine (copper), CA Leviathan mines, CA Fire Road mine, New Brunswick, Canada Copper basin, TN Unnamed site, Alpine, CA Sunshine mine, ID Inactive copper mine, VT Zortman Landusky–Swift Gulch site, MT Wellington–Oro water treatment plant Lava Cap mine, CA Toby Creek, PA Friendship Hill, PA

		Argo tunnel, CO Cement Creek, CO American tunnel, CO Confidential, gold and silver mine, CO
Chemical stabilization phosphate and biosolids treatment	SMW	Orono–Dunweg, MO Ore Hill mine, NH
Constructed treatment wetland	MIW	Bark Camp. PA Commerce/Mayer Ranch, OK Copper basin, TN Dunka mine, MN Keystone, CA Hartshorne/Whitlock, OK Ohio, Multiple sites Tecumseh, AML Site 262, IN Valzinco mine, VA
Diversionary structures	MIW	Leviathan mine, CA Copper Hill Bingham Canyon mine Stowell mine, CA Tar Creek, OK
Electrocoagulation	MIW	Hydro-met LLC, SD
Electrokinetics	SMW	Electrokinetic remediation at Alameda Point, Alameda, CA: http://costperformance.org/profile.cfm?ID=5&CaseID=5 Electrokinetic extraction at the unlined chromic acid pit, Sandia National Laboratories, NM: http://costperformance.org/profile.cfm?ID=246&CaseID=246 Electrokinetics at site 5, Naval Air Weapons Station, Point Mugu, CA: http://costperformance.org/profile.cfm?ID=189&CaseID=189 In situ electrokinetics remediation at the Naval Air Weapons Station, Point Mugu, CA: http://costperformance.org/profile.cfm?ID=188&CaseID=188
Excavation and disposal of solid mining waste	SMW	Annapolis lead mine, MO Lava cap mine, NV Potosi area, MS Shiny Rock mine, WA Valzinco mine, VA
In situ biological treatment	MIW and SMW	Sequatchie Valley coal mine, TN
In situ treatment of mine pools and pit lakes	MIW	Red Oak coal mine, OK
Ion exchange	MIW	Soudan mine, MN

Microbial mats	MIW	Fort Hood, TX Tennessee Valley Authority, AL
Passivation technologies	SMW	Golden Sunlight mine, MT
Permeable reactive barrier systems	MIW	ITRC PRB-4, 2005: Nickel Rim mine site, Sudbury, Ontario, Canada ITRC PRB-4, 2005: Monticello Mill tailings site, Monticello, UT Permeable reactive wall treatment of acid mine leachate at the Basin Luttrell pit, Ten Mile Creek site, Lewis and Clark County, MT: www.kemron.com/Documents/Hard%20Rock%20Presentation.ppt#315,1,Slide
Phytotechnologies	MIW and MSW	Ely copper mine, VT, phytosequestration Kerramerican NPL, ME, phytohydraulics Magmont mine, MO, phytosequestration Black Butte mercury mine, OR, phytosequestration Gribbons basin, MI, phytosequestration, phytohydraulics Valzinco mine, VA, phytosequestration Copper basin, TN, phytosequestration Sequatchie Valley coal mine, TN, phytosequestration, phytohydraulics Bark Camp, PA, phytosequestration, phytohydraulics Annapolis lead mine site, MO, phytosequestration UP mines, MI, phytosequestration Boston Mill, AZ
Pressure-driven membrane separation technologies	MIW	Bingham Canyon mine groundwater project, zone A sulfate plume, Kennecott south zone, UT Coal mine, southwestern, Pennsylvania
Reuse and reprocess technologies	MIW and SMW	Tar Creek (operable unit 4) Potosi mine, MO

[a]MIW, mining-influenced water; MSW, mining solid waste.

Recycling of Mine Sites

Although some mine sites have significant environmental challenges, ecological revitalization can occur and contaminated mine sites can be recycled into community assets (U.S. EPA, 2009). Many former mine sites with ponds have been converted from brownfield properties to natural habitats with lakes and wetlands. Even golf courses have been developed as part of mine reclamation activities. Ecological revitalization provides a variety of positive environmental, economic, and social impacts.

The positive impacts of ecological revitalization are as follows (Interstate Technology and Regulatory Council, 2006; U.S. EPA, 2009):

- Repairs damaged land
- Improves soil health
- Supports diverse vegetation

- Reduces erosion
- Sequesters carbon
- Controls landfill leachate
- Protects surfacewater and groundwater from potential contamination
- Helps remove stigma associated with prior waste site
- Enhances property values and raises tax revenue (www.epa.gov/superfund/programs/recycle/pdf/method.pdf)
- Provides passive recreational opportunities
- Contributes to a green corridor or infrastructure

References

Interstate Technology and Regulatory Council, 2006. Planning and Promoting Ecological Land Reuse of Remediated Land. ECO-2. ITRC and Wildlife Habitat Council, Washington, DC. http://www.itrcweb.org/Documents/ECO-2.pdf.

Interstate Technology and Regulatory Council, 2011. Mining Waste Treatment Technology Selection, Technology Overviews. http://www.itrcweb.org/miningwaste-guidance/technology_overviews.htm

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

Case Study 1

Property name and location: Palmerton zinc pile, Superfund site, Palmerton, Pennsylvania.

Regulatory agency: U.S. EPA Region 3, Philadelphia, Pennsylvania.

Property type: Mining site.

Site description: The Palmerton zinc pile site is the area of a former primary zinc smelting operation. The site encompasses the borough of Palmerton and surrounding areas, Blue Mountain, a large smelting residue pile called the Cinder Bank, and much of the valley. For nearly 70 years, the New Jersey Zinc Company deposited 33 million tons of slag at the site, creating a cinder bank that extends for $2\frac{1}{2}$ miles and measures over 100 ft high and 500 to 1000 ft wide. The smelting operations emitted huge quantities of heavy metals throughout the valley. As a result, approximately 2000 acres on Blue Mountain, which is adjacent to the former smelters, have been defoliated, leaving a barren mountainside. Soil on the defoliated area of the mountain has contaminated the rainwater flowing across it. The runoff and erosion have carried contaminants into Aquashicola Creek and the Lehigh River. Approximately 850 people live within 1 mile of the site; the population of the town of Palmerton is approximately 5000. The Palmerton Water Company has four production wells at the foot of Blue Mountain that supply water to the towns of Palmerton and Aquashicola; to date these wells have not been affected by contaminants from the site (U.S. EPA, 2011).

Remediation method: Former smelting operations resulted in soil and shallow groundwater contamination by heavy metals, such as lead, cadmium, and zinc and created a defoliated area on the

adjacent Blue Mountain, a cinder bank, and additional defoliation along Stoney Ridge. Heavy metals were being transported to nearby stream segments through erosion. Biosolids were applied to accelerate revegetation of the defoliated areas, to stabilize the area, reduce soil erosion caused by wind and surface water, and increase evapotranspiration to prevent percolation of water and contaminants to the groundwater. In addition, a system was installed to divert surface water around the cinder bank and treat leachate before discharge to the creek.

Revitalization/reuse component: For the Blue Mountain revegetation, site managers constructed a self-sustaining meadowland because of minimum metal uptake from the plants. Tree species with high metal uptake were removed. For the cinder bank revegetation, the team used a grass seed mixture that included a nitrogen-fixing legume to maintain nitrogen fertility without the need for fertilizer.

Challenges: Attempting to establish forestland at the site was extremely challenging because of competition from grasses, animal grazing, and insects. Some grass species were not desirable because of metals uptake. Use of sludge as a soil amendment caused a negative public perception. Forestland was ultimately abandoned in favor of meadowland. The types of grass seeds were replaced with those having minimal metals uptake. Sludge application was replaced with mushroom compost.

References

U.S. EPA, 2011. Palmerton Zinc: Current Site Information. Mid-Atlantic Superfund Files. http://www.epa.gov/reg3hscd/npl/PAD002395887.htm.

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

Case Study 2

Property name and location: DeSale Restoration, Butler County, Pennsylvania.

Regulatory agency: Pennsylvania Department of Environmental Protection, Harrisburg, Pennsylvania.

Property type: Mining site.

Remediation method: Early mining on the Middle Kittanning coal bed left a barren landscape with severely degraded acid mine drainage issuing from the toe of the spoil. The discharge emanating from this site affects approximately 3 miles of Seaton Creek, the major tributary affected most heavily by abandoned mine drainage within the Slippery Rock Creek Watershed headwaters. The site, about 8 acres of barren spoil, was reclaimed using 35,058 tons of alkaline material, circulating fluidized-bed coal ash from December 1999 to May 2000. The passive treatment system was installed in six weeks March to May 2000 and included four components: anoxic collection system with inlet control structure, two vertical-flow ponds operated in parallel, a settling pond/wetland complex, and a horizontal-flow limestone bed.

Water is collected using a French drain type of subsurface collection system. The water is directed into the top of the two vertical-flow ponds operating in parallel. The water flows vertically (top to bottom) through a 6-in. layer of spent mushroom compost and a 4-ft layer of limestone (3000 tons, 1500 tons per pond, and the American Association of State Highway and Transportation Officials No. 1 limestone aggregate, 90% $CaCO_3$ equivalent. The treatment medium generates alkalinity.

Two tiers of perforated plastic pipe installed in the aggregate collect the water flowing through the

vertical-flow ponds. The treated water discharges through the outlet control structures into a ¾-acre settling pond or wetland. This settling pond allows periodic flushing of vertical-flow ponds to remove accumulated metal precipitates (primarily iron and aluminum). The wetland facilitates additional iron oxidization and settling of iron and aluminum precipitates. Finally, the water passes through a horizontal-flow limestone bed, adding alkalinity and removing a portion of manganese, which discharges through an 8-in. perforated underdrain (Stream Restoration, Inc., 2006).

Revitalization/reuse component: A passive treatment system was used to capture and treat acid mine drainage and included an anoxic collection system, vertical-flow ponds, a settling pond and wetland complex, and a horizontal-flow limestone bed.

Challenges: In addition to creating a treatment wetland complex, 11 miles of streams that were once devoid of aquatic organisms due to acid mine drainage have been documented to support robust fish populations.

References

Stream Restoration, Inc., 2006. DeSale Phase I Restoration Projects, overseen by the Pennsylvania Department of Environmental Protection, Knox District Mining Office, Slippery Rock Watershed Coalition. http://www.srwc.org/projects/desale.php.

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

Case Study 3

Property name and location: Chisman Creek, York County, Virginia.

Regulatory agency: U.S. EPA Region 3, Philadelphia, Pennsylvania.

Property type: U.S. EPA Superfund mining site.

Site description: Between 1957 and 1974, a local contractor deposited more than 500,000 tons of fly ash from Virginia Power's Yorktown Power Station in abandoned sand and gravel pits on the Chisman Creek property. Fly ash is a sootlike by-product that results from burning fossil fuels such as coal and petroleum coke. In 1980, complaints from local citizens about discolored well water prompted state agencies to investigate the area. Results of the sampling showed heavy metal contamination in Chisman Creek, in the groundwater under the disposal areas, and in various on-site ponds. The metals included nickel, vanadium, arsenic, beryllium, chromium, copper, molybdenum, and selenium. The Chisman Creek site is 15 miles north of Norfolk, Virginia, and consists of three parcels of land covering 27 acres. Over 1200 households are within 2 miles of the site. Chisman Creek, a tributary of the Chesapeake Bay, is a 4200-acre coastal watershed that starts as a small stream and ends as a broad tidal estuary. The estuary, on-site ponds, and land were used by local residents for recreational purposes (U.S. EPA, 2011).

In 1983, the EPA added the site to its list of hazardous waste sites needing cleanup. Working with the local community, state agencies, and Virginia Power, the EPA developed a two-part cleanup strategy. In 1986, Virginia Power began the first part of the cleanup, which targeted the fly ash pits and contaminated groundwater. It extended public water lines to 55 homes with contaminated well water; covered the fly ash pits with clay, clean soil, and vegetation; and installed a groundwater treatment system at the oldest and deepest pit to collect and treat water trickling through the cap. To prevent use of the groundwater,

Virginia Power filed deed restrictions with the county. The second part of the cleanup plan targeted the three on-site ponds, a freshwater tributary stream, and the Chisman Creek estuary. Virginia Power relocated a 600-ft portion of the tributary to lessen the possibility of contact with the fly ash disposal areas and protect the aquatic ecosystem. Finally, it established a program to monitor ground- and surface-water quality for the ponds, the tributary, and the estuary (U.S. EPA, 2011).

In 1986, a 12-member stewardship committee comprising local residents and business representatives, a geology professor from the nearby College of William and Mary, a NASA scientist, and environmental professionals was formed to oversee cleanup and redevelopment of the site. Local residents were eager for the cleanup but wanted to continue to use the area for recreation. A sports park was the perfect solution. As part of the cleanup, Virginia Power built a site cap that would also serve as the foundation for playing fields, and leveled and graded the site so that York County could build park structures and sod the fields. York County also purchased a lighting system that was installed by Virginia Power during the final stages of the cleanup. The Chisman Creek sports park opened on May 4, 1991, with about 300 local residents, media, Virginia Power officials, and EPA, state, and county personnel on hand to enjoy the festivities. The 13-acre park has two lighted softball fields, rest rooms, and a parking lot. The second park, the 28-acre Wolf Trap Park, features four soccer fields, rest rooms, a parking lot, two ponds, and the county's memorial tree grove (U.S. EPA, 2011).

Remediation method: Groundwater and surface water were contaminated with heavy metals from the disposal of fly ash. The cleanup plan eliminated contact with the fly ash and contaminated water, restored groundwater, and protected nearby wetlands.

Revitalization/reuse component: The site is being reused as a recreational complex, including ponds and the county memorial tree grove. The site cleanup also protects nearby ponds, a creek, and an estuary, and it is part of a large water quality improvement that has led to reopening of the Chisman Creek estuary for private and commercial fishing.

Challenges: Not specified.

References

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. EPA, 2011. Crisman Creek Case Study. Mid-Atlantic Superfund Files. http://www.epa.gov/superfund/programs/recycle/live/casestudy_chisman.html.

Case Study 4

Property name and location: Black Warrior–Cahaba Rivers Land Trust, Alabama.

Regulatory agency: U.S. EPA Region 4, Atlanta, Georgia.

Property type: Brownfield mining site.

Site description: As far back as the late nineteenth century, Jefferson County in Alabama became a hub of coal, iron, and limestone mining activities. Coal coking, the processing of coal to form a condensed, nearly smoke-free fuel, was performed on a large scale in Jefferson County in support of the burgeoning Birmingham, Alabama steel and pig iron business. However, in the decades after World War II, technological advances and a general decline in U.S. steel production led to decreased demand for these

industries, and many of Jefferson County's coal-producing and other industrial properties were abandoned. Recognizing that these idle properties, many of which were located along scenic Five-Mile Creek, could provide significant recreational value if restored, a partnership emerged in 2002 to transform this former industrial region into a 27-mile greenway with parks and paths. The partnership is led by the Black Warrior–Cahaba Rivers Land Trust, an Alabama conservation organization focused on land along rivers and streams. At the time of this writing, assessments funded by U.S. EPA grants have been conducted on nine properties within the project area. These include the Sloss property, a 300-acre property used heavily for coal mining and coking and later for strip mining in what is now close to downtown Birmingham, Alabama. Although portions of the site were reforested in the 1980s, approximately 20 of the original, turn-of-the-century coke ovens still exist on the Sloss property in good condition. The mining of coal, low-grade iron ore, and limestone contributed to Birmingham's growth as a southern pig-iron and steel center in the late nineteenth and early twentieth centuries until about the mid-1970s, when newly enacted environmental regulations for air and water pollution accelerated the closure of all but the most modern and efficient plants.

This is a brownfield site and environmental assessments discovered lead and other heavy metals contaminating the soil. More than $54,000 in additional assessment funds was leveraged from local, private, and other federal entities. About $3 million was spent for land acquisition totaling more than 350 acres, and $4.2 million for recreational park development, water quality studies, and remediation of the creek (U.S. EPA, 2006). Community “stream cleanup” events were conducted, drawing hundreds of people, and involved local schools in water monitoring and other scientific activities related to the Creek greenway project.

Cleanup is ongoing at the 300-acre Sloss property, which will eventually be part of the Five-Mile Creek greenway project's 27-mile network of parks, open space, and trails. The partnership plans to preserve the property's remaining coke ovens as reminders of the area's industrial and mining history. While it could take as long as 20 years for the entire greenway project's completion, many of the project's targeted, former industrial areas have already been cleaned up and made available to appreciative local communities as natural and recreational land (U.S. EPA, 2006). Tours are now available of the Sloss furnaces, and artists lease shop space on the site of the former pig iron manufacturing plant. In 1981 the Sloss furnace site was designated a National Historic Landmark (Figure 35.1). The success of the Sloss furnace museum illustrates community support for the reuse of a former mining or industrial property as an educational and research facility which features science exhibits and a movie on early iron and steel technologies together with tours of the historic grounds.

Figure 35.1 Sloss furnace National Historic Landmark, now a tourist attraction in Birmingham, Alabama. (Courtesy of James A. Jacobs.)

Remediation method: Soils were contaminated with lead and heavy metals. Remediation solutions were developed with the community and included a recreational park and community stream cleanup events.

Revitalization/reuse component: A former industrial region was transformed into a 27-mile greenway with parks and paths along Five-Mile Creek.

Challenges: It could take 20 years to complete the entire greenway project. Many of the targeted former industrial areas have been cleaned up and made available to communities as natural and recreational land.

References

U.S. EPA, 2006. Sloss Property. Brownfields at-a-glance brochure. Black Warrior–Cataba Rivers Land Trust, AL Assessment Grant. http://water.epa.gov/learn/training/wacademy/upload/fultondale_al_BRAG.pdf, p1.

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

Case Study 5

Property name and location: Cherokee County, Galena, Kansas.

Regulatory agency: U.S. EPA Region 7, Kansas City, Kansas.

Property type: U.S. EPA Superfund mining site.

Site description: The Cherokee County site is a former mining area covering about 115 square miles. It is part of a larger area sometimes called the Tri-State Mining District, which encompasses approximately 2500 square miles in southeastern Kansas, southwestern Missouri, and northeastern Oklahoma. Over 100 years of widespread lead and zinc mining created piles of mine tailings which covered over 4000 acres in southeastern Cherokee County. The mine tailings contain lead, zinc, and cadmium which have leached into the shallow groundwater. Runoff from the waste piles also moves contaminants into nearby streams. Acidic waters in mine shafts throughout the site, chat piles, tailings impoundments, surface waters in the mine pits, and streams draining the site contain significant concentrations of lead, zinc, and cadmium. Surficial soils are contaminated with mining, milling, and smelting wastes, exclusive of areas where remediation is now complete. Risks to public health include incidentally ingesting soil, mine wastes, and contaminated dust, or ingesting contaminated surface waters, foodstuffs, or groundwater (U.S. EPA, 2006).

Acid mine drainage containing dissolved heavy metals contributes to the transport of heavy metals into the Spring River, Short Creek, Tar Creek, Shoal Creek, and other lesser drainages and water bodies. Ecological impacts have been demonstrated, and the uppermost aquifer is contaminated. Polluted mine water also surfaces in Oklahoma's portion of Tar Creek. The former Eagle–Picher smelter near Galena was responsible for the airborne distribution of lead and cadmium in residential areas near this community. Mining and milling wastes have also been imported into residential areas throughout the site for use as fill, landscaping, and road construction materials. Wind and water action have also transported the various types of mining wastes into other areas. Some portions of the site have been fully remediated, work is ongoing in certain locations, and future actions are planned for areas not yet addressed (U.S. EPA, 2010).

Remediation method: Remediation consisted of burying surface mine wastes contaminated with lead, mercury, and cadmium in abandoned mine pits, subsidence areas, and mine shafts on site; diverting streams away from waste piles; recontouring land surface; and revegetating with native prairie grasses to control runoff and erosion.

Revitalization/reuse component: Native prairie grassland habitat encouraged the return of wildlife.

Challenges: There is a potential for cave-in of filled mine shafts after heavy rain or freezing and thawing cycles. Development in areas with a potential for cave-in or collapse has been avoided.

References

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. EPA, 2010. Site Status Report, Cherokee County, Kansas. EP ID# KSD980741862, EPA Region 7, June 17, 2010, Galena, Baxter Springs, Treece, Badger, Lawton, Waco, Crestline. http://www.epa.gov/region7/cleanup/npl_files/ksd980741862.pdf, 12 pp.

Case Study 6

Property name and location: California Gulch Superfund site, Upper Arkansas River operable unit, Leadville, Colorado.

Regulatory agency: U.S. EPA Region 8, Denver, Colorado.

Property type: U.S. EPA Superfund mining site.

Site description: At an elevation of 10,152 ft, Leadville (pop. 2800) is the highest incorporated city in the United States. Gold was first discovered along California Gulch in 1859. In the 1860s and 1870s, Leadville was the location of rich deposits of silver, gold, copper, zinc, manganese, and lead. In 1874, two veteran miners discovered lead–silver ore, and with the creation of the first smelter at California Gulch, silver was the main focus (Figure 35.2). By the 1890s, mineral mining had become more expensive. Mines were dug deeper and began to flood, forcing mining companies to dig long tunnels to drain the acidic mine drainage into sensitive desert environments. In 1987, the mine closed, but the environmental damage associated with acid mine drainage remained in the gulches below the mining areas.

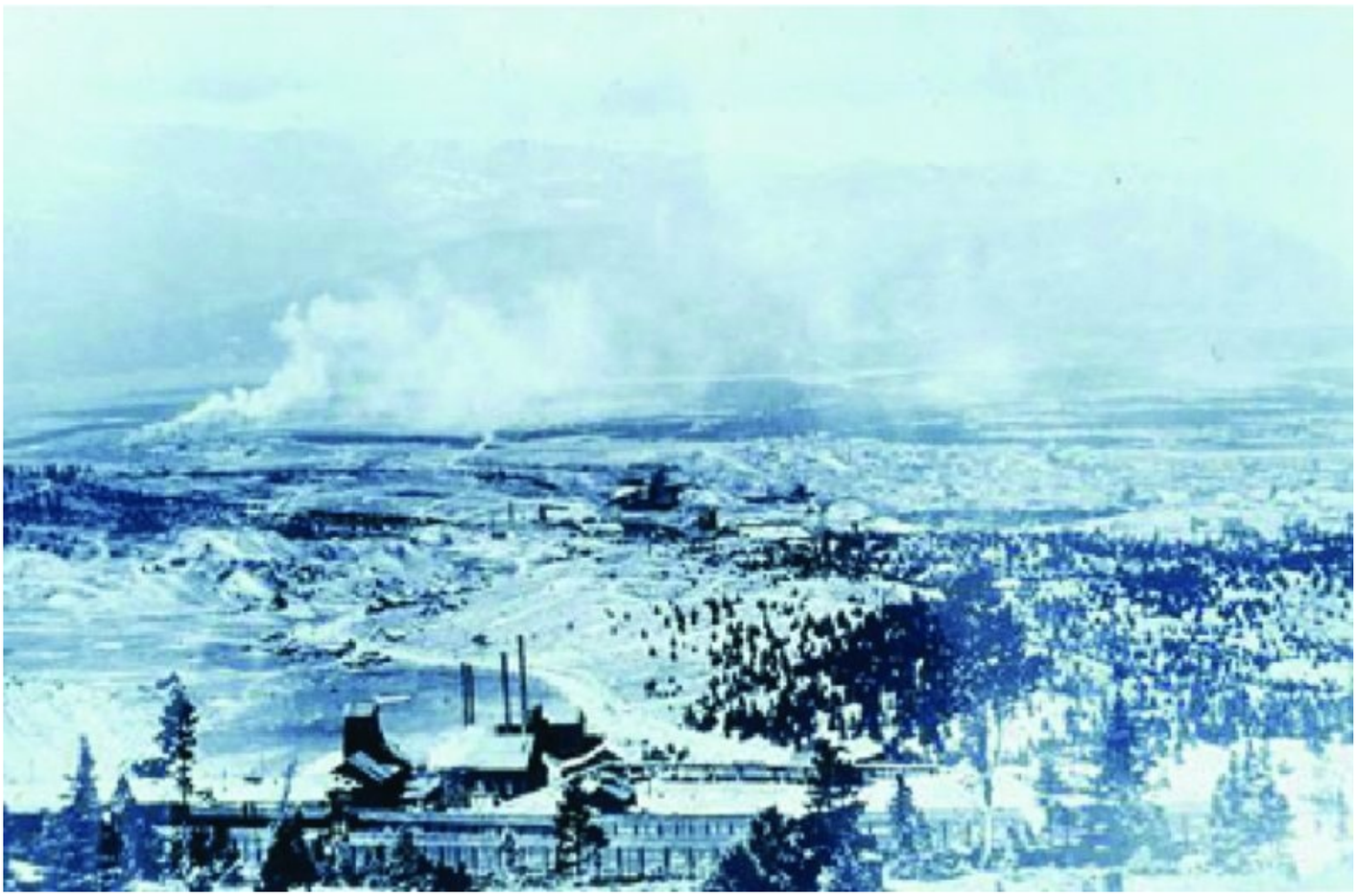


Figure 35.2 Smelters in Leadville in the early twentieth century (From U.S. EPA, 2011.)

The California Gulch Superfund Site consists of about 18 square miles in Lake County, Colorado, and includes Leadville, the highest incorporated city in the United States. Mining, mineral processing, and smelting activities in the area have produced gold, silver, lead, and zinc for more than 130 years. Mining in the Leadville area began in 1859 when prospectors working in the channels of the Arkansas River tributaries discovered gold at the mouth of California Gulch. Wastes generated during the mining and ore-processing activities contained metals such as arsenic and lead at levels posing a threat to human health and the environment. These wastes remained on the land surface and migrated through the environment by washing into streams and leaching contaminants into surface water and groundwater. The site was added to the National Priorities List in 1983, and in 1994 was divided into 12 geographically based areas, each

identified as operable units. Investigation of the site began in the mid-1980s (U.S. EPA, 2011).

Remediation method: The mining district's soil, surface water, and sediments were heavily contaminated with lead, zinc, and other heavy metals from mine tailings. Biosolids and lime were applied directly to the tailings along the Upper Arkansas River.

Revitalization/reuse component: The area along the river has been restored and supports vegetation and wildlife and is available for agricultural use and recreational use such as hiking and fishing.

Challenges: Tailings could not be excavated because of the risk of tailings entering the river and the difficulty of finding a repository for the contaminated soil. Also, replacement of topsoil would be costly. Mobilizing materials to the site was difficult, due to the elevation of the site. Water was also scarce, due to low rainfall and high elevation. Biosolids were spread over the tailings, reducing the potential for tailings to migrate to the river.

References

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. EPA, 2011. Site Status Report, California Gulch Region 8 Superfund Program, EPA Region 8, July 20, 2011. http://www.epa.gov/region8/superfund/co/calgulch/, 8 pp.

Case Study 7

Property name and location: Kennecott north and south zone sites, Salt Lake County, Utah.

Regulatory agency: U.S. EPA Region 8, Denver, Colorado.

Property type: U.S. EPA Superfund mining site.

Site description: The Kennecott site consists of two parts, north and south. The Kennecott south zone includes the Bingham mining district in the Oquirrh Mountains, about 25 miles southwest of Salt Lake City. The mountain range represents the west boundary of the Salt Lake Valley. Mining activities at the site began in the 1860s and continue to the present at the large Bingham Canyon open-pit mine. Historic mining operations produced lead, zinc, silver, copper, molybdenum, and gold ores. Kennecott Utah Copper Company (Kennecott) and the Atlantic Richfield Company (ARCO) have cleaned up mine waste dumps, mill tailings, smelter wastes, and groundwater and surface water, including wetlands, with oversight by state and federal agencies (U.S. EPA, 2011).

In 1990, EPA and the Utah Department of Environmental Quality (UDEQ) found that homes had been built on former flood plains contaminated with high levels of lead and arsenic. Kennecott and ARCO, with EPA, UDEQ, and community input, conducted studies to determine the nature and volume of the contaminated wastes. Cleanup involved eight separate subsites: Bingham Creek residential neighborhoods; Bingham Creek channel; Large Bingham Reservoir; Butterfield mine waste rock and other canyon wastes; Herriman residential neighborhoods; Lark tailings, mine waste rock, and wetlands; South Jordan evaporation ponds; and Anaconda tailings piles. Cleanup of these subsites involved digging up near-surface soil wastes with high lead and arsenic levels, and removal of the wastes to collection and storage areas. More than 25 million tons of mining wastes have been removed. Removal of the surface wastes was completed in 1999 (U.S. EPA, 2011).

The Kennecott north zone site is an industrial area at the north end of the Oquirrh Mountains and at the

south shore of Great Salt Lake, west of Salt Lake City, Utah. The site is next to the community of Magna, which has a population of 15,000. Interstate highway I-80, state highways, and rail lines pass through the site. Recreation near the site includes lakeshore swimming and wading, sunbathing, and bird-watching. Since 1906, the site has been used to process copper-, lead-, zinc-, molybdenum-, arsenic-, gold-, and silver-bearing ores. The wastes produced contain hazardous substances, including heavy metals. Sludge and soils are contaminated, as are surface water and groundwater that affect wetlands between the site and the beach. Kennecott Utah Copper Company is cleaning up the site with oversight by state and federal agencies. The cleanup approach for the site has been addressed in stages: early actions and long-term phases. The first actions focused on removal of surface contamination found during modernization of the smelter and refinery. The second early action involved soils in Magna. The analytical results indicated that these soils do not pose a health threat to the public. The long-term phases focus on cleanup of the wastewater treatment plant sludge ponds, wetlands, and soils. Methods of groundwater treatment for the site are currently being investigated (U.S. EPA, 2011).

Remediation method: Soil and groundwater were contaminated with mining wastes, including sulfates and heavy metals. Soil was removed, and groundwater was pumped and treated in the mine's tailings slurry line (U.S. EPA, 2009).

Revitalization/reuse component: Open space, wetlands, and wildlife habitat were created during site restoration. A residential area was also created.

Challenges: Not specified.

References

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. EPA, 2011. Site Status Reports, Kennecott North and South, EPA Superfund Program, EPA Region 8, January 19, 2011. http://www.epa.gov/region8/superfund/ut/kennecottnorth/index.html (north zone), 3 pp.; http://www.epa.gov/region8/superfund/ut/kennecottsouth/ (south zone), 3 pp.

Case Study 8

Property name and location: Milltown Reservoir Sediments, Milltown, Montana.

Regulatory agency: U.S. EPA Region 8, Denver, Colorado.

Property type: U.S. EPA Superfund mining site.

Site description: From the 1860s until well into the twentieth century, mineral- and arsenic-laden waste from mining activities in the region flowed into the headwaters of the Clark Fork River. The river, a renowned trout fishery, was located in one of the richest mining areas in the world. As contaminated sediments and mine-mill wastes moved downstream, many of these sediments accumulated behind the Milltown Dam near Milltown, Montana, polluting the local drinking water aquifer and threatening the health of local ecosystems. Completed in 1908, approximately 6.6 million cubic yards of contaminated sediments accumulated behind the dam over time (U.S. EPA, 2011b). In 1981, Missoula County health officials discovered arsenic contamination in drinking water wells in Milltown, Montana. The wells were located near the Milltown dam and reservoir. To protect public health, the EPA provided an alternative water supply to affected area residents and in 1982 proposed listing the site on the National Priorities List (NPL) for cleanup under Superfund. The site was made final on the NPL in 1983 (U.S. EPA, 2011a).

Following initial environmental investigations, EPA listed the site on the National Priorities List in September 1983. The Milltown Reservoir/Clark Fork River Superfund site is divided into three parts, or operable units: Clark Fork River, Milltown water supply, and Milltown reservoir sediments, which is the focus of this case study. In turn, the site is part of a larger regional effort addressing much of the Clark Fork River's watershed, including the Warm Springs ponds, Anaconda smelter, and Butte/Silver Bow Creek Superfund sites, which together comprise one of the largest toxic waste cleanups in the country. The EPA selected a remedy for the Milltown reservoir sediments site in its 2004 record of decision. Components of the remedy included construction of a bypass channel at the reservoir, removal of contaminated sediment in the reservoir (2.2 million cubic yards), off-site disposal and use of the contaminated sediments as vegetative capping media, removal of the Milltown Dam, continuation of a replacement water supply program and implementation of temporary groundwater controls until the Milltown aquifer recovers, and long-term monitoring of surface water and groundwater. The EPA worked with the state of Montana from the outset to coordinate the site's remedy with the state's restoration plan for the area. The state's plan, developed in conjunction with the U.S. Fish and Wildlife Service, the confederated Salish and Kootenai tribes, and site trustees, is designed to restore the confluence of the Clark Fork and Blackfoot rivers near the Milltown Dam to a naturally functioning, stable system. Other coordination activities led to the removal of the Stimson Dam (located on the Blackfoot River) and additional state restoration actions to provide additional habitat and stream bank improvements (U.S. EPA, 2011b).

Remediation method: Six million cubic yards of mining waste that had piled up at the base of the Milltown Dam was poisoning the reservoir and affecting drinking water. A new drinking water system was installed at the site (U.S. EPA, 2009).

Revitalization/reuse component: In addition to adding a new drinking water system, 2.5 miles was added to existing hiking trails in Missoula to complete a loop around the University of Montana and Missoula's waterfront (U.S. EPA, 2009).

Challenges: Not specified.

References

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. EPA, 2011a. Site Status Report, Milltown Reservoir Sediments, Milltown, Montana, EPA Superfund Program, EPA Region 8, April 29, 2011. http://www.epa.gov/region8/superfund/mt/milltown/, 6 pp.

U.S. EPA, 2011b. Integrating the “3 Rs”: Remediation, Restoration and Redevelopment, The Milltown Reservoir Sediments Site and Misssoula County, Montana, EPA Region 8, April 2011. http://www.epa.gov/region8/superfund/mt/milltown/2011ReadyForReuse FactSheet.pdf, 14 pp.

Case Study 9

Property name and location: Silver Bow Creek and Warm Springs ponds, Butte, Montana.

Regulatory agency: U.S. EPA Region 8, Denver, Colorado.

Property type: U.S. EPA Superfund mining site.

Site description: The site became contaminated when, from 1915 to 1980, miners in Butte dumped

wastes into four nearby streams. These waterways carried an astounding 19 million tons of tailings and other mining wastes into the headwaters of the Clark Fork River. Over time, these tailings began to take a heavy toll on the environment. In 1956, in an attempt to slow the harmful effect of the tailings on the Clark Fork River and its headwaters, the Anaconda Copper Company dug three collection ponds on what is now called Warm Springs ponds. These ponds eventually became severely polluted. In 1983, the site was placed on the EPA's list of priority hazardous waste sites needing cleanup. In 1990, after several removal actions, the EPA teamed with ARCO (which had recently bought the Anaconda Mining Company) to clean up the area further. Working together, they removed more than 450,000 cubic yards of sediments from the ponds and installed a comprehensive water treatment system. ARCO also agreed to pay $1.7 million to create 400 acres of new wetlands in the area (U.S. EPA, 2011).

Today, the wetlands at Warm Springs ponds is an important habitat for migrating Canadian geese and breeding areas for dozens of songbirds and ospreys. To improve existing habitat, ARCO built nesting platforms to protect waterfowl from predators. But Warm Springs ponds isn't just wetlands. Today, as a result of additional work by ARCO, the area boasts bike paths, a self-guided walking tour, numerous fishing sites, and an area for dog training. Further improvements, such as a footbridge and additional fishing areas, are expected in the years to come (U.S. EPA, 2011).

Remediation method: Remediation included excavating sediment contaminated by copper-mining activities and installing a water treatment system (U.S. EPA, 2009).

Revitalization/reuse component: Extensive wetlands are now home to a variety of wildlife. Nesting platforms were built to protect birds. The wetlands are also used for recreation, such as fishing, hiking, and biking (U.S. EPA, 2009).

Challenges: Not specified.

References

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. EPA, 2011. Site Status, Report, Silver Bow Creek and Warm Springs Ponds, Butte, Montana, EPA Superfund Program, EPA Region 8, August 9, 2011. http://www.epa.gov/superfund/programs/recycle_old/success/1-pagers/bowcrk.htm, 1 p.

Case Study 10

Property name and location: Summitville Mine, Colorado.

Regulatory agency: U.S. EPA Region 8, Denver, Colorado.

Property type: U.S. EPA Superfund mining site.

Site description: The Summitville mine site is located 25 miles south of Del Norte, Colorado at an elevation of 11,500 ft above sea level in the San Juan Mountains of southwestern Colorado. The mine site is situated south of Wightman Fork, a tributary of the Alamosa River, about 2 miles east of the Continental Divide. Mountain peaks surrounding the mine site range between 12,300 and 12,700 ft in elevation. The historic town of Summitville is just to the north of the mine site on the other side of Wightman Fork. The area is traditionally subject to severe winters with heavy snowfall accumulating on steep slopes. Snow may often remain on the ground until late spring or early summer, providing water in quantities sufficient

to keep streams, including Wightman Fork, flowing year-round, and acting as a continual source of water entering the soil. Gold and silver mining began at Summitville around 1870. Large-scale open-pit mining began at the site in 1984. The mine operator, Summitville Consolidated Mining Corp., Inc. (SCMCI), used cyanide heap leaching to extract precious metals from the ore. In this process, ore excavated from the mountain was crushed and placed onto the clay and synthetic-lined heap leach pad (HLP). A sodium cyanide solution was then applied to leach out gold and silver. Almost immediately after its construction in 1986, a leak was detected in the HLP. SCMCI abandoned the site and announced that it was filing for bankruptcy in December 1992. The EPA immediately assumed responsibility for the site as an emergency response. On May 31, 1994, Summitville was placed on the National Priorities List of Superfund sites (U.S. EPA, 2011).

Remediation method: Gold mining released cyanide and acidic mine water to the Alamosa River. Cleanup activities include permanently stabilizing the site and reversing the effects of mining on the river (U.S. EPA, 2009).

Revitalization/reuse component: The Alamosa River and tributaries flow through wetlands, forested and agricultural land, and into the Terrace Reservoir, which supplies irrigation water to livestock and farms. The site has been revegetated with grasses that promote the recolonization of native plants. The river, which was void of life because of contamination, now supports some types of aquatic life (U.S. EPA, 2009).

Challenges: Not specified.

References

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. EPA, 2011. Site Status Report, Summitville Mine, Colorado, EPA Superfund Program, EPA Region 8, January 25, 2011. http://www.epa.gov/region8/superfund/co/summitville/, 6 pp.

Case Study 11

Property name and location: Harmony mine and mill, Baker, Idaho.

Regulatory agency: U.S. EPA Region 8, Denver, Colorado.

Property type: U.S. EPA Superfund mining site.

Site description: The Harmony mine is a former copper mine and milling facility that operated between 1916 and 1931. The site is located near Baker, Idaho, in northeastern Lemhi County, approximately 15 miles southeast of Salmon. The property is near the headwaters of Withington Creek and consists of approximately 330 acres of both private and National Forest System land. During production the mill tailings were deposited directly into Withington Creek. Two wooden dams were used as retention walls for the mine waste tailings pile. The south fork of Withington Creek flows into the Lemi River approximately 8 miles downstream of the site. The Lemhi River flows an additional 10 miles to its confluence with the Salmon River in Idaho. The entire area is considered a sensitive environment, and the tailings deposits are visible in the creek bed for up to 2.5 miles downstream from the tailings piles (U.S. Forest Service, 2011).

Remediation method: A diversion ditch was created and pipes laid to divert Withington Creek from

tailings piles. After they were dry, 10,000 yd^3 of tailings were excavated and hauled to a repository location. A sedimentation pond was also constructed below the tailings pile to catch any runoff that occurred. Tailings were then capped with a 2-ft layer of compacted rock followed by a 1-ft layer of uncompacted rock (U.S. EPA, 2009).

Revitalization/reuse component: Where the tailings were removed, the area was graded, a stable creek bed with the ability to withstand large debris flow was constructed, and disturbed areas were seeded. Withington Creek is a designated cold-water community and salmonid spawning habitat for the endangered chinook salmon (U.S. EPA, 2009).

Challenges: Not specified.

References

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. Forest Service, 2011. Harmony Mine: Salmon-Challis National Forest Brochure. http://www.fs.fed.us/r4/resources/minerals/mine_cleanup/completed_projects/harmony.pdf, 2 pp.

Case Study 12

Property name and location: West Page swamp is part of the Bunker Hill mining and metallurgical complex National Priorities List site, Shoshone County, Idaho.

Regulatory agency: U.S. EPA Facilities Raritan Depot, Edison, New Jersey.

Property type: U.S. EPA Superfund mining site.

Site description: The Bunker Hill Superfund site, located in northern Idaho and eastern Washington, was listed on the National Priority List in 1983. It is one of the largest and most complex Superfund sites in the country. The site includes mining-contaminated areas in the Coeur d'Alene River corridor, adjacent floodplains, downstream water bodies, tributaries, and fill areas. The West Page swamp is part of the larger Bunker Hill Superfund site. Mine tailings were capped near the northeastern corner of the West Page swamp. They also constructed a small dam or weir for the East Page and West Page swamps. The weir will help maintain a steady water level all year round and keep metals from moving downstream. Several more projects will be built next year in preparation for the future diversion of water from the Page sewage treatment plant into the West Page swamp. Millions of tons of mill tailings, mine waste rock, and ore concentrates are spread across the site. Mining contamination has affected more than 166 river miles of the Coeur d'Alene River corridor, adjacent floodplains, downstream water bodies, tributaries, and fill areas (U.S. EPA, 2001, 2011). A photo from the EPA from 2005 depicts the restored West Page swamp (Figure 35.3).

Figure 35.3 Restored West Page swamp. (From U.S. EPA, 2011.)

Remediation method: Remediation included constructing a cap over soil contaminated with lead and zinc tailings. The cap consisted of biosolids compost and wood ash (U.S. EPA, 2009).

Revitalization/reuse component: The wetland is now a wildlife habitat (U.S. EPA, 2009).

Challenges: Stakeholders were concerned that remediation is only a short-term solution because contaminants were not completely removed from the site. Groundwater and surface water wells were installed and are being monitored quarterly or annually (U.S. EPA, 2009).

References

U.S. EPA, 2001. Superfund Fact Sheet, Bunker Hill, Kellogg, Idaho, January 2001, 6 pp.

U.S. EPA, 2009. Ecological Revitalization: Turning Contaminated Properties into Community Assets. EPA 542-R-08-03. U.S. EPA, Washington, DC, 80 pp.

U.S. EPA, 2011. EPA Promotes Ecological Revitalization at Superfund Sites, Superfund Program, August 9, 2011. http://www.epa.gov/superfund/accomp/news/restoration.htm, 1 p.

36
SUSTAINABLE AQUACULTURE USING TREATED AND UNTREATED MINE WATER FROM COAL MINES

KENNETH J. SEMMENS AND JAMES A. JACOBS

Water is a valuable by-product of the coal industry. Although it may be considered “impaired,” other industries can and do make use of it. The power industry may use water in the cooling process or to generate electricity directly. Agriculture and its smaller cousin, aquaculture, require significant volumes of water and show promise. Fish culture can be used as a postmining land use to save on reclamation costs. Treated water from mine drainage is a potential resource capable of economic benefit, which has been demonstrated clearly in West Virginia, Maryland, and Pennsylvania. Treated water originating from coal mines in the eastern U.S. Appalachian Mountains has been used to produce rainbow trout in an economical manner for almost two decades. In this chapter we summarize the systems that were utilized over a period of about 10 years (Semmens and Miller, 2003). Five case studies are examined for activities that occurred over the past 10 years. Descriptions are written in the past tense for that reason. Net pens and raceways have been used at three acid mine discharge treatment plants. Four commercial facilities utilizing groundwater flowing from coal mines in West Virginia have produced over a million pounds of rainbow trout and arctic char during the past 10 years.

Introduction

Water originating from active or abandoned mines may be the most important natural resource available for the development of aquaculture in West Virginia. In a mine water inventory conducted in 1994 (Jenkins et al., 1995), it was estimated that an aggregate volume of 118,000 gal/min was available throughout West Virginia for development by the aquaculture industry. Further, it was reported that 53% of the volume available was suitable, without additional treatment, for the production of rainbow trout. As of 2011, for every high-flow mine site in West Virginia that could be used as part of aquaculture production facilities, there are two mine sites with high-water-flow capability that are not being used for fish production. More detailed descriptions of production and production economics are available Miller, 2008; Miller and D'Souza, 2008, 2009).

Making use of the water available from West Virginia mining operations required the development of methods and technologies to manage risk and provide a consistent water volume with suitable quality for the production of trout. Heinen (1996) concluded correctly that mine waters are suitable for growing trout after treatment. However, the need for consistent water quality was stressed as being critical for the health of the fish and subsequent consumer confidence. Treated and untreated water originating from coal mines in Appalachia have been used to produce harvestable-size salmonids for the past two decades. There are several aquaculture facilities in three states where salmonids are grown for the food and recreational markets using this water source.

Ponds

In addition to the benefits of recycling of treated water and postmining reclamation, water storage ponds can be used at reclaimed coal mine sites for a variety of purposes. Presently, treatment ponds are not

designed with aquaculture in mind. Although ponds can be used with cages or net pens, manure from the fish can accumulate and increase the risk to fish health. Some treatment ponds are not operated continuously and are therefore not suitable for aquaculture since most fish producers rely on a constant flow of water. Heating and cooling of the water by natural processes influence potential growth of the fish and thus profitability. Reliability of the treatment process and the associated risk of fish mortality is also a concern.

Fish Selection

Many varieties of fish are grown in aquaculture, each with its own preference for water temperature and water quality. The most common species considered for mine water is trout. It is utilized for both food and recreation and is the most widely grown fish in the region. Groundwater temperatures in the region are near the fish's optimum of 59°F. Like a natural spring, groundwater flowing from mines has a stable temperature that allows year-round production of trout. Other fish may benefit from water quality. For example, striped bass (*Monrone saxatilis*) and their hybrids benefit from the calcium levels in mine water treated with calcium hydroxide. Channel catfish (*Ictalurus punctatus*), koi carp (*Cyprinus carpio*), and yellow perch (*Perca flavescens*) grow and survive well, but water temperatures may be suitable for growth during just a few months of the year. Largemouth bass (*Micropterus salmoides*) and hybrid bluegill (bluegill sunfish, *Lepomis macrochirus*×green sunfish, *Lepomis cyanellus*) are not species recommended for grow-out in a flow-through system utilizing treated mine water. Even when water temperatures were suitable for growth, they did not respond to water with high levels of dissolved solids.

Rainbow trout (*Onchorhynchus mykiss*) of various strains, brook trout (*Salvelinus fontinalis*), brown trout (*Salmo trutta*), and splake (*Salvelinus namaycush*×*Salvelinus fontinalis*) have been grown in both treated and untreated mine water. Rainbow trout were reared in treated mine water in an initial proof-of-concept study (Viadero and Tierney, 2003). The fish can withstand summer water temperatures in the Fahrenheit range mid- to upper 70s, (20 to 26°C). Commercial production is not recommended for water temperatures exceeding 70°F. Figures 36.1 to 36.6 show various fish grown in water from coal mines.

FIGURE 36.1 Rainbow trout grown in treated mine waters. (Courtesy of K. Semmens.)

FIGURE 36.2 Brown trout. (Courtesy of K. Semmens.)

FIGURE 36.3 Brook trout. (Courtesy of K. Semmens.)

FIGURE 36.4 Hybrid striped bass. (Courtesy of K. Semmens.)

FIGURE 36.5 Striped bass. (Courtesy of K. Semmens.)

FIGURE 36.6 Yellow perch. (Courtesy of K. Semmens.)

Striped bass (*Monrone saxatilis*) and hybrid striped bass (white bass, *Morone chrysops*×striped bass, *Monrone saxatilis*) are popular as sport fish, due to their aggressive feeding behavior. Additionally, there is increasing demand for hybrid striped bass as a food fish. Northeastern U.S. markets in particular are expanding, which is beneficial for West Virginia. Finally, hybrid striped bass are tolerant of a wide range of temperatures and salinities.

Elements of Fish Production

Trout production facilities can be considered aquatic feedlots where fish convert high protein feed pellets into flesh. Water is the medium in which this process occurs. During this process, oxygen is consumed and carbon dioxide, ammonia, and fish manure is produced.

Water Quality

Abundant sources of well-oxygenated water with a pH between 6.5 and 8.5, and stable water temperatures between 40 and 70°F are required for production of trout. Rainbow trout will survive temperatures between 33 and 78°F (Wedemeyer, 2001), but production is not recommended at temperatures above 70°F. Groundwater sources maintain stable temperatures throughout the year between 50 and 60°F. This allows the grower to feed fish all year long, something not possible in surface waters.

At the standard environmental temperature of 15°C or (59°F), rainbow trout can be expected to increase total length at the rate of 1 in./month. Dissolved oxygen levels must be above 60% of saturation and nonionized ammonia levels below 0.03 mg/L if there is to be no effect on growth. Trout in hard water systems (>250 mg/L) use less energy on osmoregulation than do trout in soft water (<100 mg/L) and will have more energy available for growth or coping with stress (Klontz, 1991). Heinen (1996) reviewed accepted water quality for rainbow trout (Table 36.1)

TABLE 36.1 Water Quality Parameters Suitable for Growing Rainbow Trout

Parameter	Recommended Range
pH	6.5 to 8.5
Alkalinity (mg/L as $CaCO_3$)	10 to 400
Sulfates (mg/L)	<850
Total hardness (mg/L as $CaCO_3$)	10 to 400
Fe (mg/L)	<0.1
Al (mg/L)	<0.087
Mn (mg/L)	<1.0

Cost of Production

The economics of production is related primarily to the efficiency of the system and market price. Two of the most predictable and significant variable costs are fish and feed. Feed cost to produce a 1-lb fish is related to the conversion rate and cost of the feed. Current prices for trout feed may range from 50 to 60 cents/lb. Considering that trout require from 1.2 to 1.7 lb of feed for 1 lb of gain, feed costs are expected to be between 60 cents and $1.02 for each pound of fish grown.

Fingerling costs will vary greatly depending on season, fish size, and volume purchased. They can be expected to range from about 13 cents each for a 3-in. fingerling (20,000-unit minimum order) to about 50 cents each for a 4- to 5-in. fingerling (5000-unit minimum order). Fingerling cost for each market-size trout will be related to initial cost and survival rate. Managerial experience, water quality, and facility design will influence survival. Given a survival rate between 80 and 90%, fingerling cost per pound of market-size fish produced will be between 14.4 and 62.3 cents.

Feed and fingerling costs for producing about 1 lb of trout can be expected to range from a low of 75 cents to 164 cents. If one were to sell to the processing plant at a price of $1.50/lb, there would be between 14.3 and 75 cents to cover all costs other than feed and fingerlings for each pound of fish produced. If one were to sell to a more limited recreational market at $2.00/lb, there would be between 35 cents and $1.25 to cover all costs other than feed and fingerlings for each pound of fish produced. Labor costs, production volume, and overhead (including interest and principal on investment) are frequently a function of facility design and market strategy. As such, facility design will frequently determine the potential profit for a fish production facility. This brief exercise is intended to point out the importance of capital investment and its influence on overhead and the profitability of a trout production system.

Suitable infrastructure (seed stock, feed, processing plant, market demand) exists to support continued growth of this industry. Rainbow trout are the predominant freshwater species cultured in this region, but other species of trout, and arctic char, are also grown. It is estimated that nearly 4 million pounds can be

produced if 30% of available mine water is utilized for this purpose (Jenkins et al., 1995). This report describes the production system at five locations utilizing treated and untreated mine water. For 2011, a dressed rainbow trout would sell for about $5.00/lb at a local West Virginia farmers' market. Live rainbow trout to stock ponds and streams sell for $2.00/lb or more plus delivery. Striped bass is about the same price of $5 dressed, with head either on or off, and a fillet with rib bones is $13/lb. Catfish were priced by the piece based on a price per pound of $6. The average weight of $8 fish was 0.67 kg and the average weight of $6 fish was 0.5 kg. The fish had been filleted with a yield of about 34% from live fish to skinless boneless fillet. Niche farmers in 2010 received higher prices, as smoked rainbow trout reached $16/lb (Miller and Semmens, 2010). All the fish have a shelf life of 7 days.

Untreated Groundwater from Coal Mines

In southern West Virginia, groundwater flowing from coal mines is suitable for growing trout without chemical treatment. During the past 10 years there were two commercial businesses operating four facilities utilizing water from coal mines that did not require chemical treatment.

Case Study 1

This case began in 1994 and is located near Beckley, West Virginia. It was the first commercial production facility in the region based on groundwater flowing from a coal mine. The mine closed in 1959. The two production facilities relied on gravity flow of aerated mine water to grow food-size rainbow trout. The water temperature remains between 55 and 56°F as it is collected from an underground area of approximately 5000 acres. Water from the source is gravity fed to tanks after passing through a degassing tower. Inside the production facility, water passes through large fiberglass tanks and into concrete raceways before being discharged into a stream. As such, it is a flow-through system relying on gravity to move water without pumping. Pure oxygen is utilized to supplement the oxygen requirements for the fish.

The flow rate at the larger of the two production facilities is 2800 gal/min at high flow and 1000 gal/min at low flow, with an average flow rate of 1900 gal/min. Minimum flow is an important limiting factor for the continuous production of food fish. The larger of the two production facilities had 22 large tanks (23 ft in diameter with depth between 5 and 10 ft) for the production of food fish, 48 small tanks (2 m in diameter) for the production of fingerlings (Figure 36.7), and facilities to hatch eggs. Four times each year eyed trout eggs are purchased to produce fry which grow into fingerlings. The smaller of the two production facilities for this case had 10 large tanks devoted to the production of food-size fish weighing between 1.25 and 1.5 lb. The flow rate at the smaller of the two production facilities varied from 400 to 1200 gal/min. Concrete raceways are efficient for fish production (Figure 36.8).

FIGURE 36.7 Tanks for the production of rainbow trout fingerlings (Courtesy of K. Semmens.)

FIGURE 36.8 Tanks have been replaced by concrete raceways for the production of rainbow trout. (Courtesy of K. Semmens.)

The aquaculture company represented in this case produced about 200,000 lb of rainbow trout at these facilities for its processing plant near Sophia, West Virginia and purchased additional fish as needed. The products were sold primarily to institutional markets, resorts, and grocery store warehouses. In a yield verification trial, the survival rate observed for 6- and 8-in. fish was 90 and 95%, respectively. There were between six and eight exchanges of tank volume each hour. Between 4 and 10 L of oxygen was injected into each production tank each minute. Approximately 1.3 lb of fish feed was required for each pound of gain. Fish in the tank system were harvested at a density approaching 2 lb/ft^3. Production ranged from 93 to 133 lb per gallon per minute of flow on an annual basis (Semmens et al., 2003). Water quality parameters are presented in Table 36.2. The water quality parameters from this facility was similar to those of other fish-growing production facilities in the region, which are spring fed. The most notable difference is the presence of iron.

TABLE 36.2 Water Quality in Production Tanks for Case Study 1

Parameter	Operating Levels
Temperature	56°F
Oxygen (supplemented as required)	7 mg/L minimum
pH	7–7.5
Alkalinity (mg/L as $CaCO_3$)	190
Hardness (mg/L as $CaCO_3$)	80
Iron (mg/L)	0.35
Total dissolved solids (mg/L)	285

The facility design in this case was not optimal. Fish are difficult to grade and harvest in tanks with a water depth of 10 ft. Material has built up inside the pipes at the larger of the two fish production facilities, constricting water flow. Management wanted to increase the volume and efficiency of dissolving oxygen in water as it enters the large grow-out tanks. Since 2005, the round fiberglass tanks with a singles water use have been replaced by rectangular concrete raceways where water flows from one raceway to another for a series of eight uses. A combination of improved management and improved facility design has improved production to 400,000 lb annually.

Case Study 2

This case in West Virginia involves a limited liability company formed in 1999. In 2000, a third party joined as an equity partner. Two facilities were constructed, one as a hatchery for fingerling production and a second as a grow-out facility. These facilities were staffed with 10 people. The grow-out facility was a $2.5 million capital investment designed by aquaculture design professionals.

Arctic char (*Salvelinus alpinus*) was chosen as the culture species. Niche markets were expected to pay a higher price for arctic char than for rainbow trout. Two of the four strains of arctic char tested grew rapidly and required little grading. Two-pound fish were produced from fingerlings in 15 months. The production facility was designed to produce 500,000 lb of market-size fish annually (Savage, 2003).

The recirculating design used in the fish grow-out facility was much more sophisticated than that of the flow-through system used in Case Study 1. The Case Study 2 grow-out facility required only 500 gal/min to operate (Figure 36.9). Make up water requires no pretreatment except degasing before it enters the system. It is drawn from an abandoned coal mine and gravity fed through 1 mile of 12 in.-diameter pipe to the facility.

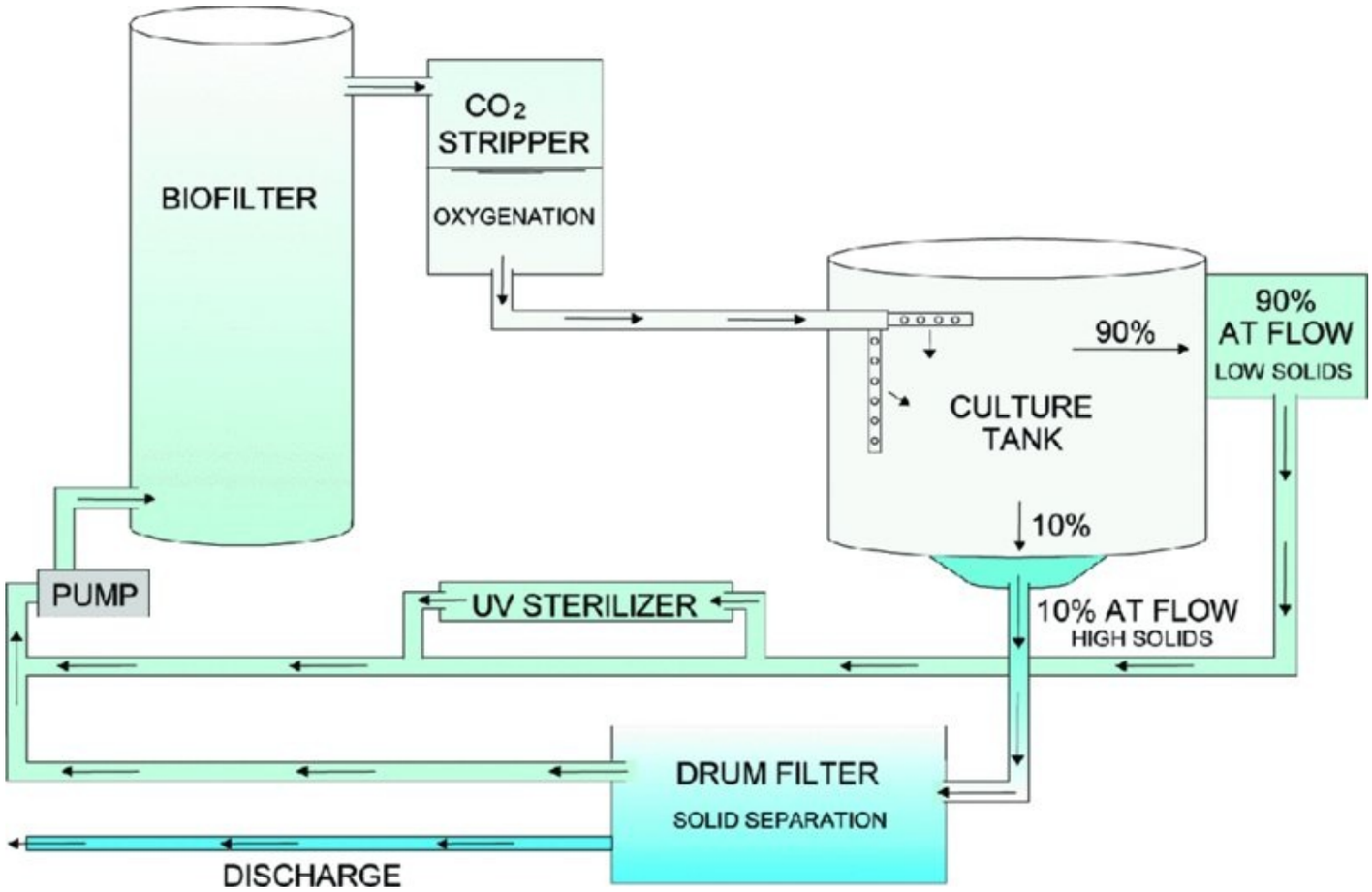


FIGURE 36.9 Recirculating aquaculture system components showing the path that water takes through major components within one type of recirculating system. (From Timmons et al., 2002.)

The fish grow-out facility was broken into three modules. Each module consists of one 30-ft-diameter circular tank, four 20-ft-diameter tanks, and the water treatment components. All modules are housed within a single building. Water flows from each culture tank out two separate drains. The side drain receives about 95% of the flow and is recirculated. Water from the side drain passes through a 90-µm drum filter to remove solids. Fluidized sand biofilters are used to convert ammonia and nitrite into nontoxic forms. After leaving the biofilter, carbon dioxide is stripped out and oxygen concentrations are increased with pure oxygen as water passes through a low-head oxygenator. Ozone is added to the flow to clarify the water. At times during the warm summer months, the water is chilled. The center drain takes about 5% of the flow and is not recirculated. This flow contains much of the solid waste produced by the fish. It passes through a drum filter to further concentrate the solid waste. Solids are incinerated and the effluent is discharged into an aerated lagoon.

Treated Groundwater from Coal Mines

Oxidized pyrite and a lack of alkaline buffering capacity creates acid mine water containing high levels of dissolved metals. This condition is commonly found in the northern part of West Virginia, and is usually treated with aeration, lime, and flocculants before passing through a one or more settling ponds (Figure 36.10). Integrating a fish production system at the end of the water treatment system has proven feasible in three locations. Doing so takes advantage of infrastructure investment and labor resources (D'Souza et al., 2003).

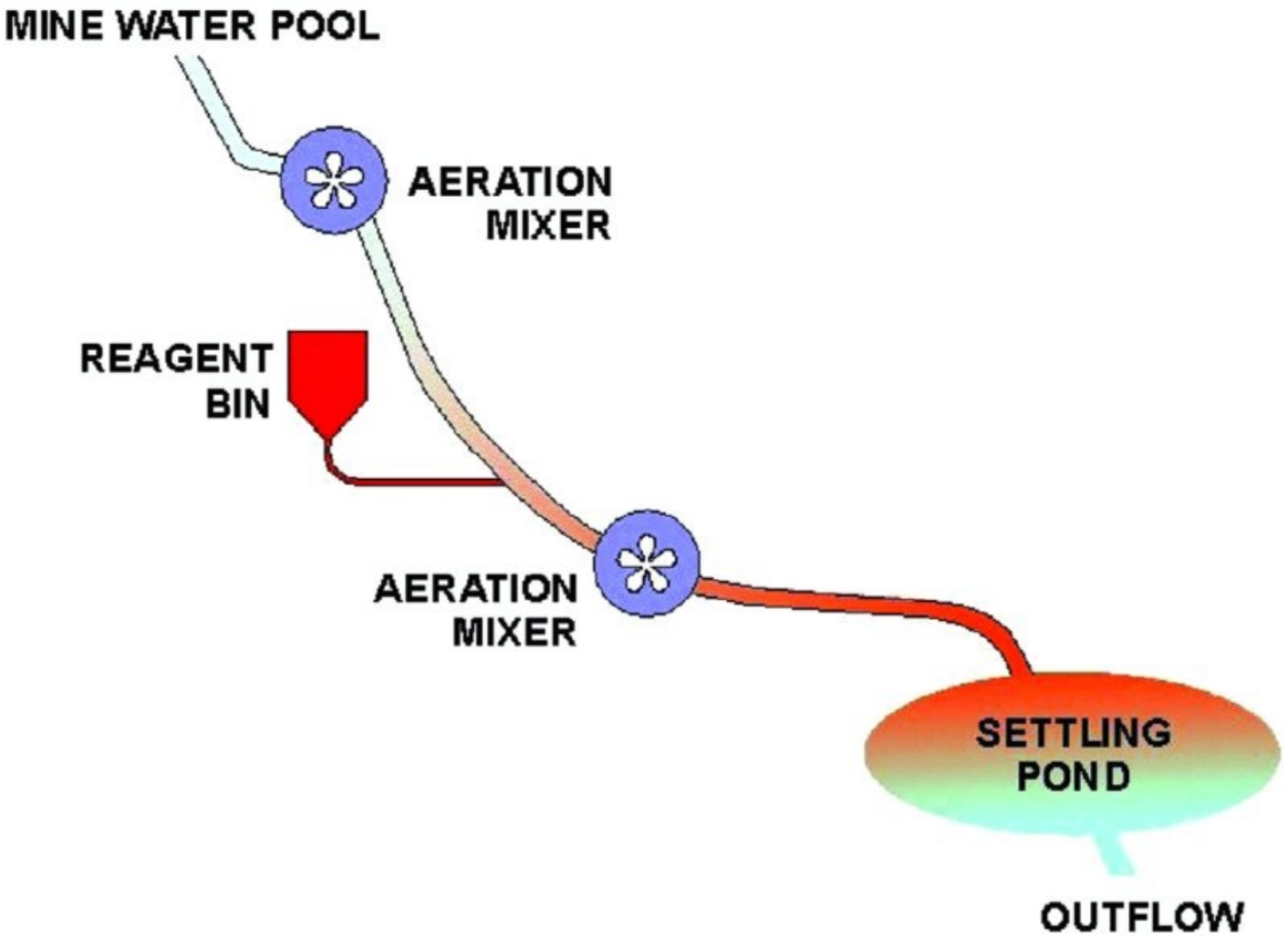


FIGURE 36.10 Treatment process for an acid mine discharge plant.

Case Study 3

This case in Maryland was a private–public partnership with a coal company and the Maryland Department of Natural Resources Freshwater Fisheries Division that pioneered development of a net pen system for trout production in the discharge of an acid mine discharge treatment plant near Oakland, Maryland. The coal company operated a drift mine that entered an outcrop of the Freeport coal seam. Working sections of the mine were approximately 2.5 miles from the mine entrance, with a depth of cover of 600 ft. Conveyor belt lines transported raw coal to the surface, where the preparation plant cleaned the coal of impurities before loading the treated coal on rail or trucks for transportation to the market. Water that pools in lower elevations of the mine was pumped to an underground sump and then to the surface and treated at the acid mine discharge treatment plant. Dual high-density sludge treatment systems at the plant were capable of treating 3000 gal/min.

Between 4.6 and 9.9 million gal/day were treated at the acid discharge treatment plant (Table 36.3). Temperature varies seasonally from 12 to 17°C and the pH increased from an average of 6.5 to 8.0 through the treatment process. Total dissolved solids (TDS) of nearly 2000 mg/L was much higher than in the untreated mine water used at the facilities in Case Study 1 or Case Study 2. Sulfates in this Case averaged 1100 mg/L and exceed the 850 mg/L level recommended in Table 36.1. Total iron and manganese were also of concern, as levels averaged 0.22 and 0.21 mg/L, respectively.

TABLE 36.3 Water Quality at the Case Study 3 Acid Mine Discharge Treatment Plant

	Raw			Effluent		
Parameter	**Mean**	**High**	**Low**	**Mean**	**High**	**Low**
Flow (million gal/day)	6.4	9.9	4.6	6.4	9.9	4.6
Temperature (°C)	14	17	12	14	17	12
Oxygen (mg/L)	—	—	—	7.6	8	7.4
pH	6.5	7.1	5.8	8	8.3	7.5
Alkalinity (mg/L as $CaCO_3$)	5	10	0	96	120	80
Total iron (mg/L as $CaCO_3$)	53	133	12	0.22		
Manganese	2.9	4.8	2.7	0.21	0.59	0.15
Sulfate	1100	1710	800	1100	1710	800
Total dissolved solids (mg/L)	1825	—	—	—	1965	

Scientists with the environmental department of the coal company contacted the Maryland Department of Natural Resources (DNR) and developed a collaboration in 1993 to determine if trout could be grown in the acid mine discharge effluent. A small number of rainbow and brown trout were grown successfully. In 1994, a formal agreement was signed in which the Maryland DNR supplied the trout fry, net pens, and food, while the coal company supplied treated water, facilities, and personnel assistance. Permitting was handled through a modification of the existing NPDES permit (Ashby and Dean, 1995).

Net pens of varying mesh size were suspended to a depth of 9 ft in the water flow. These measured 15 by 20 ft and were supported by a platform that allowed access on all four sides (Figure 36.11). Solar-powered automatic feeders mounted above the water surface fed fish in each pen on a predetermined schedule. Fingerlings were stocked into the nets when they are about 3 in. long (60 fish/lb) and fed a high-protein pelleted diet. Fish were sampled biweekly to estimate weight accumulation and determine feeding rate adjustments. Nets were cleaned by pulling sections up and hosing with a water spray.

(a) (b)

FIGURE 36.11 Net pens at (a) the case 3 acid mine discharge treatment plant and (b) the case 4 facilities. (Courtesy of K. Semmens.)

Trout grown at this facility were thought to be nearly twice as large as trout in other DNR hatcheries and may have exceeded 1 lb each. This performance was attributed to optimal growing temperatures at the acid mine discharge plant during winter months. Trout produced at this acid mine discharge treatment plant were stocked for recreation in the streams of western Maryland between March and June of each year of the study. This collaboration and its facilities continued to evolve. It may have been the first location to grow trout in effluent from an acid mine discharge treatment plant and was certainly the longest operating trout production facility utilizing water from an acid mine discharge plant in the region. Facilities were modified to increase annual production capacity to 48,000 lb/yr.

Case Study 4

This case in southwestern Pennsylvania builds on work conducted in the Case Study 3 acid mine discharge treatment plant and attempted to utilize the water resource as one strategy to offset reclamation and water treatment costs (Koenig and Blankenship, 2002). Located near Point Marion, Pennsylvania, this mine water treatment plant was capable of treating 6 million gal/day (4200 gal/min). Normally, there was a continuous discharge of 1000 to 2000 gal/min of water saturated with oxygen at a temperature between 40 and 65°F. The polishing pond receiving the treated water was 10 to 12 ft deep with a surface area of approximately 1 acre.

Like Case Study 3, the company behind the present case first conducted a test with a small number of fingerlings and were encouraged with the results. In 2002, a floating dock system supporting net pens was installed in the polishing pond (Figure 36.11). Each pen is 10 ft wide, 40 ft long, and 6 ft deep and provides about 2000 ft^3 of rearing area suspended 5 ft off the pond bottom. The nylon net mesh was knotless and coated with plastic to minimize abrasion to the fish. Nylon ropes at intervals beneath the mesh along their width allow the nets to be pulled up and divided into eight compartments for sampling and harvest.

In October 2001, 10,000 rainbow trout fingerlings were stocked into the system. The fish selected were a heat-tolerant strain of rainbow trout available through a local commercial supplier. The fish survived and grew well. Annual mortality rate was estimated at 1.5% and an average of 1.44 lb of feed was required to

grow a pound of fish. A series of harvests through the production period of 340 days yielded 6480 lb of fish. Fish grew to 0.04 to 1.36 lb average weight and were sold into the recreational market.

Case Study 5

West Virginia University (WVU) installed an experimental modular composite raceway system below a 17-acre impoundment that receives treated mine water from a facility operated by a coal company about 15 miles west of Morgantown, West Virginia. An average of 2135 gal/min of water was pumped from two underground mine pools, aerated, treated with hydrated lime, and aerated again before flowing back into the impoundment.

The traditional raceway design commonly used for trout production by government agencies and private growers was selected. Flowing-water systems are used where there is a continuous flow of water and where the elevation allows water to drop for aeration between production units. The system was installed by WVU and contained paired tanks each 3 ft wide and 30 ft long (Figure 36.12). Approximately 500 gal of water is aerated as it drops 3 ft between each of the four levels. The system required no power, as the water flowed by gravity, no supplemental oxygen, and only part-time labor on a daily basis. Only two weeks of work was required to clear the site and install the modular composite system.

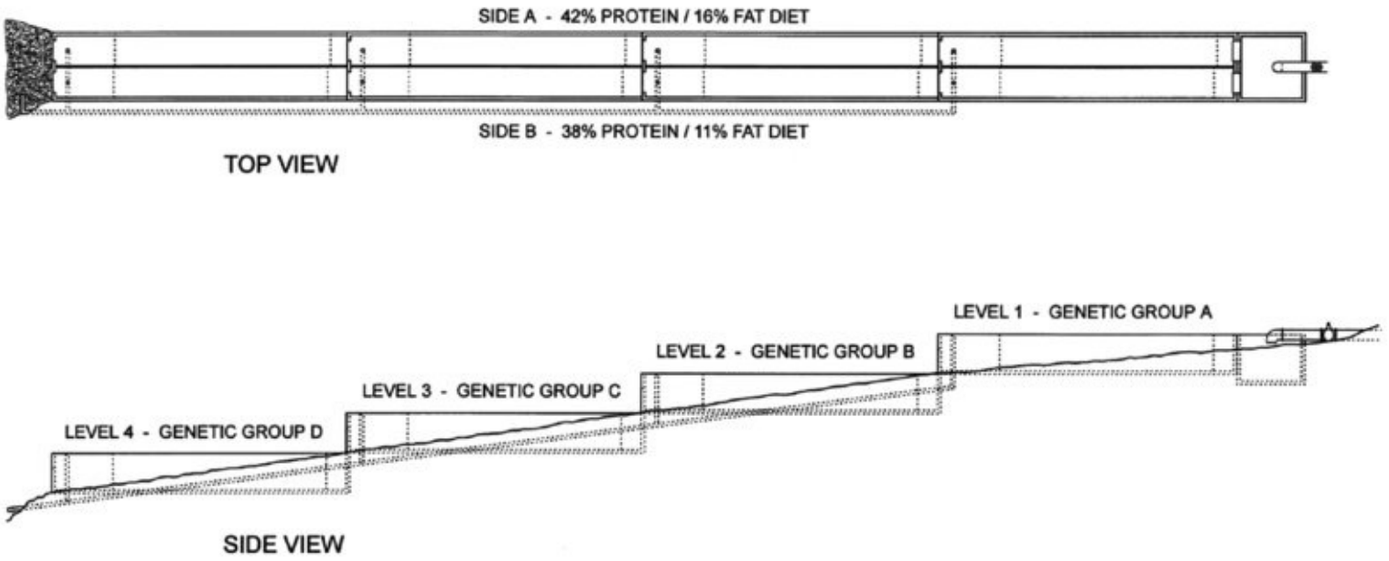


FIGURE 36.12 WVU raceway system and experimental treatments.

The average concentrations of dissolved metals was evaluated for this case, including Fe, Al, Mn, Ca, Mg, and SO_4, which was sampled monthly. Although the average measured concentration of metal ions at the outlet often exceeded the standards recommended, the active concentration was actually below the standard, with the exception of magnesium (Viadero and Tierney. 2003). Total dissolved solids were very high at 4000 mg/L, twice as high as in Case Study 3 and 14 times higher than in Case Study 1. The associated ionic strength of this treated mine water effectively reduced the “active” concentrations of metal ions in solution, making the water more suited to fish production. Table 36.4 shows the water quality entering the raceway.

TABLE 36.4 Water Quality Entering the Case Study 5 Raceway System

Parameter	Average	Range
pH	8.2	7.82–8.46
Alkalinity (mg/L as $CaCO_3$)	307	279–340
Sulfates (mg/L)	3517	3096–3795
Total hardness (mg/L as $CaCO_3$)	1585	1463–1664
Fe (mg/L)	0.3	0.15–0.31
Al (mg/L)	0.19	0.06–0.30
Mn (mg/L)	0.73	0.36–1.18

Investigators working at this site quickly determined that this water source is suitable for the production of trout on a seasonal basis (Viadero and Tierney, 2003). Research began in October 2002 to evaluate diet, genetics, water quality, product quality, and whether or not the accumulation of metals rendered the fish unsafe to eat. Information collected to date indicate that the fish are safe to eat and that some genetic groups grow faster than others. It was determined that the most limiting water quality parameters affecting the use of treated mine water at this site are high summer water temperature and the concentration of metals. The settling impoundment supplying this system exchanged heat such that both winter and summer temperatures were not suited for year-round trout production. Large fingerlings were stocked in October and harvested as food-size fish in late spring. During the winter, water temperatures were as low as 35°F and the pond surface was frozen. Although trout survived this cold water, they do not convert feed well and grow slowly. At temperatures of 40°F they will grow less than 0.3 in./month. As water temperatures rise in the spring, the fish grow well and densities exceed 5 lb/gal. As water temperature passes 70°F, mortality will increase. Fish are harvested from the system and stocked again the following fall.

Rainbow trout grown in mine water at this site did not have a significantly increased stress response or contaminant levels higher than those of control fish (Danley and Mazik, 2004). The productivity of trout grown in treated mine water was similar to that of fish grown in other commercial operations and was consistent with predictions made using existing computer models. Thousands of pounds of fish have been grown in this treated mine water since 2002. The facility is not a fish hatchery, in that fish are not spawned and fingerlings are not produced. All fish are stocked as fingerlings and grown to a harvestable size. Initially, only trout were grown, but other species have since been stocked in the system. These fish species include rainbow, brook, and brown trout; hybrid striped, striped, and largemouth bass; hybrid bluegill; channel catfish; and yellow perch. Various strains of rainbow trout performed best on a seasonal basis when water temperatures were below 20°C. One strain reputed to be more temperature tolerant survived and grew through the summer when water temperature approached 25°C (Figure 36.13). Hybrid striped bass and striped bass survived and grew well in the system, presumably due to the level of dissolved solids in the water, particularly calcium (about 430 mg/L). Yellow perch grew as expected and survived well. Largemouth bass and hybrid bluegill did not grow or survive as well as expected. Catfish survived and grew well in the summer months. Catfish of total length above 20 cm survived winter better than did small catfish (<15 cm). It is apparent that the primary limiting factor to production of most species is water temperature. Warm-water species (bass, catfish, bluegill) have only four months of warm temperatures for growth. It is also noteworthy that mature trout grown in the system have released eggs and milt.

FIGURE 36.13 Angler with trout caught from an acid mine drainage polishing pond. (Courtesy of K. Semmens.)

This research has shown that this resource can be used to raise healthy fish for stocking public waters and for human consumption. Results from flesh analysis have shown that these fish are safe to eat and provide a healthy form of protein for consumption (Tierney and Viaderp, 2002). The West Virginia DNR successfully stocked tagged hybrid striped bass, raised in the high-TDS low-chloride waters of the Arkwright mine treated water, in the Morgantown pool of the Monongalia River.

The volume of treated mine water in West Virginia will increase in the future (Donovan and Leavitt, 2004). Production facilities for trout or other species located in mine water treatment sites could provide economical and sustainable fish production. This production could be used for local consumption as well as for stocking local streams for improved recreational opportunities.

Conclusions

Each of the five case studies representing fish farming projects in three eastern states (West Virginia, Maryland, and Pennsylvania), illustrated a different aquaculture production system, each having advantages and disadvantages. Raceways required large volumes of water and allowed moderate levels of production in an efficient format. Trout grew at densities of 6 lb/gal or more in each tank. Production rates of about 100 lb per gallon per minute of flow had been shown feasible in commercial trout farms

using surface or spring water with serial reuse and good management. Labor for feeding, grading, and harvesting in the rectangular tanks frequently required only part-time commitment. Raceways were designed and managed for removal of up to half of the solid waste produced by the fish. Case Study 1 can be considered a flowing-water system with round tanks instead of rectangular raceways and oxygen supplementation.

Net pens suspended in existing impoundments are relatively inexpensive and easily tended. They did not utilize the water flow efficiently from a production perspective. For example, the Case Study 3 facility produced about 11 lb of fish for each gallon per minute of flow in 2003. The Case Study 4 facility expected to produce about 10 lb per gallon per minute in 2003. Like raceways, net pens are labor efficient and may be operated with existing or part-time labor. Solid waste from the fish is not recovered, however, and will accumulate on the pond bottom. As production increases it will eventually pollute the pond and must be removed.

Recirculating systems support large volumes of fish with a relatively small water source. The Case Study 2 grow-out facility is expected to support annual production of 500,000 lb with a water source of approximately 400 gal/min. In the process of cleaning up the water for reuse, wastes are removed. This technology is effective at growing fish but is capital, knowledge, and labor intensive. Given this format, it only makes sense to grow a higher-value product such as arctic char in these systems. Other growing formats were also of interest. For example, the company featured in case 4 was developing a floating raceway system to complement its net pens. This design was expected to have many of the advantages of traditional raceways, including removal of solid waste.

The profitability of aquaculture in mine water is influenced by the same limitations as those of aquaculture using surface or spring water. Existing investment in infrastructure (e.g., a polishing pond, roads, security fence) may lower the cost of a budding aquaculture enterprise. Cost of feed, fingerlings, and survival to market will largely determine variable costs and is expected to range from $0.75 to $1.64/lb. Facility design will influence investment cost, labor, production volume, and very likely, expected market price. For example, selling 20,000 lb of 1-lb trout into the recreational market can be expected to bring about $0.50/lb more than selling the same fish to a processing plant. Selling 100,000 lb of 1-lb trout into the recreational market may not be feasible, leaving the processing plant as the only market available. It is not expected that aquaculture will be a highly profitable venture but, rather a risky venture with moderate profitability best undertaken by those who enjoy the work.

Aquaculture research has shown that the recommended water quality parameters suitable for rainbow trout should be modified. Trout are surviving and growing in these systems where water quality parameters exceed recommended limits. Ionic strength may have a role in this phenomenon (Tierney and Viadero, 2002). Investigators at each facility utilizing treated mine water to grow trout conducted a test with a small number of fish as the project began. Success built upon success, and facilities were expanded. Tests were also conducted at acid mine drainage treatment plants where fish did not survive. In one case, water was not treated on a continuous basis and the temperature in the polishing pond was too high to support trout year round. In another case, the treatment process maintained a pH value too high to support fish survival reliably.

Utilization of groundwater from coal mines for aquaculture is working and can be expected to benefit from existing investment in infrastructure. The tangible benefits of aquaculture are shown in Figure 36.13. At present, commercial production of trout and arctic char as a food fish in West Virginia is dependent on these water sources.

Water scarcity and famines are global problems that affect billions of people. Regarding the use of treated

mine water worldwide, we are witnessing the integration of two critical industrial processes: resource extraction and local food production. Given the precious nature of our natural surface water and groundwater sources throughout the world and the need for locally grown healthful food, environmental stewardship, and economic development, it only makes sense to continue developing technology and strategies for aquaculture to utilize the mine water resources.

References and Suggested Reading

Ashby, J., and Dean, J.M., 1995. Treated mine drainage effluent benefits maryland and West Virginia fishermen. http://www.gcnet.net/mettiki/extra2.html.

Danley, M., and Mazik, P.M., 2004. Physiological Overview of Rainbow Trout Grown in Reclaimed Mine-Water. American Society of Mining and Reclamation, Morgantown, WV, April 18–22.

Donovan, J.J., and Leavitt, B.R., 2004. The future of mine water discharges from underground coal mines of the Pittsburgh coal basin, WV. In: Proceedings of the American Society of Mining and Reclamation, Lexington, KY, pp. 518–528.

D'Souza, G., Miller, D., Semmens, K., and Smith, D., 2003. Mine water aquaculture as an economic development strategy: linking coal mining, fish farming, water conservation and recreation. Journal of Applied Aquaculture. vol. 15, pp. 159–172.

Heinen, J., 1996. Water Quality Criteria, Uptake, Bioaccumulation, and Public Health Considerations for Chemicals of Possible Concern for Culture of Rainbow Trout. Conservation Fund's Freshwater Institute, Shepherdstown, WV.

Jenkins, M., and Hankins, J.A., 1996. West Virginia Mine Water Inventory Site Summary. Technical report prepared by the Conservation Fund's Freshwater Institute, Shepherdstown, WV.

Jenkins, M., Wade, E., Fletcher, J., and Hankins, J., 1995. Economic Analysis of Non-Traditional Water Resources for Aquaculture in West Virginia. Conservation Fund's Freshwater Institute, Shepherdstown, WV. Technical report prepared for the Appalachian Regional Commission, Contract 940-101 WV-11529–94-I-302-0411.

Klontz, G.W., 1996. A Manual for Rainbow Trout Production on the Family-Owned Farm. Nelson & Sons, Inc., Murray, UT.

Koenig, L., and Blankenship, C.K., 2002. Propagation of rainbow trout in treated mine water at the Warwick Project. IWC 02-37. Presented at the International Water Conference.

Miller, D., 2008. Using aquaculture as a post-mining land use in West Virginia. Journal of the International Mine Water Association. vol. 27, no. 2, pp. 122–126.

Miller, D., and D'Souza, G., 2008. Economic analysis of an alternative raceway system. Northeast Regional Aquaculture Center.
http://www.nrac.umd.edu/files/Annual%20Reports/annual_report_2008.pdf p. 17

Miller, D., and D'Souza, G., 2009. Plastic tanks compare well to concrete tanks in trout trial. Global Aquaculture Advocate, vol. 12, no. 1, pp. 53–54

Miller, D., and Semmens, K., 2010. Growing fish in high tds low chloride treated mine water. Presented

at the Upper Monongahela River Association, Monongahela River Summit V, April 19, Morgantown, WV.

Savage, T., 2003. Farming Arctic char in recirculating systems using a mine water supply at West Virginia Aqua LLC. Abstract. In: Aquaculture America, February, Louisville, KY. World Aquaculture Society, Baton Rouge, LA.

Semmens, K., and Miller, D., 2003. Utilizing mine water for aquaculture. IWC-03-24. In: Proceedings of the International Water Conference, Pittsburgh, PA, October 19–23.

Semmens, K., Delabbio, J., and Eya, J., 2003. Verifying yield at two west virginia trout farms. In: Proceedings of the National Aquaculture Extension Conference, April 7–11. Tuscon, AZ.

Tierney, A., and Viadero, R., 2002. Implications of Active Dissolved Metal Concentrations and Speciation on the Use of Treated Mine Water for the Culture of *Oncorhyncus mykiss*. West Virginia Academy of Sciences, Morgantown, WV.

Tierney, A., and Viadero, R., 2003. Implications of active dissolved metal concentrations and speciation on the use of treated mine water for the culture of *Oncorhynchus mykiss*. In: Aquaculture America, February, Louisville, KY, World Aquaculture society, Baton Rouge, LA, p. 291.

Timmons, M.B., Ebeling, J.M., Wheaton, F.W., Summerfelt, S.T., and Vinci, B.J., 2002. Recirculating Aquaculture Systems, 2nd ed. Northeast Regional Aquaculture Center 01-002. Cayuga Aquaculture Ventures, Ithaca, NY. www.c-a-v.net.

Viadero, R., and Tierney, A., 2003. Use of treated mine water for rainbow trout (*Oncorhynchus mykiss*) culture: a preliminary assessment. Aquacultural Engineering, vol. 29, no. 1–2, pp. 43–56.

Viadero, R., Tierney, A., and Semmens, K., 2004. Use of treated mine water for rainbow trout (*Oncorhynchus mykiss*) culture: a production scale assessment. Aquacultural Engineering, vol. 31 pp. 319–336.

Wedemeyer, G.A., ed., 2001. Fish Hatchery Management, 2nd ed. American Fisheries Society, Bethesda, MD.

PART V
APPENDIXES

APPENDIX A
WEB RESOURCES FOR ACID DRAINAGE ISSUES

A variety of professional societies, nonprofit groups, and community organizations are focused on acidic drainage issues and the safe redevelopment of abandoned and closed mine properties. Several of these organizations are noted below.

ADTI

The Acid Drainage Technology Initiative promotes advances in acid drainage prediction, prevention, control, sampling and monitoring, and treatment. ADTI is composed of more than 50 mine drainage experts, who develop new ideas, practical methods, and cost-effective technologies to avoid and remediate acid drainage. Information on acid drainage research results and technologies are summarized. Acid Drainage Technology Initiative, Coal Mining Sector.

http://www.aciddrainage.com/

IMWA

The International Mine Water Association shares a common interest in mine water and mine drainage issues, with professional disciplines that range from science such as chemistry, hydrogeology, microbiology, and geophysics to engineering expertise, including mining and civil engineers.

http://www.imwa.info/

INAP

The International Network for Acid Prevention produced the Global Acid Rock Drainage Guide to address the prediction, prevention, and management of drainage produced from sulfide mineral oxidation, often termed acid rock drainage, acid mine drainage or acid and metalliferous drainage, mining-influenced water, saline drainage, and neutral mine drainage.

http://www.gardguide.com/index.php/Main_Page

ITRC

The Interstate Technology and Regulatory Council in the United States is a state-led national coalition of personnel from the environmental regulatory agencies of all 50 states and the District of Columbia, three federal agencies, tribes, and public and industry stakeholders. Since 1995, the organization has focused on reducing barriers to, and speeding interstate deployment of, better, more cost-effective, innovative environmental techniques. The ITRC has a mining waste treatment technology section focused on acid mine drainage.

http://www.itrcweb.org/miningwaste-guidance/index.htm

MEND

The Mine Environmental Neutral Drainage was formed in Canada in 1989 to develop technologies to prevent and control acid drainage. The program developed by MEND is directed by a multistakeholder committee, with members from the mining industry, Canadian federal and provincial government agencies, and nongovernment organizations.

http://www.mend-nedem.org/default-e.aspx

MiWER

The Mine Water and Environmental Research Centre is a formal research center based at the Edith Cowan University Centre for Ecosystem Management (Joondalup Campus) in Western Australia. MiWER is an international team of highly qualified professional scientists with skills spanning from ecology and environmental chemistry to microbial ecology and sustainability, all with an interest in mine water focusing on researching acid drainage problems.

http://www.miwer.org/

PADRE

The Partnership for Acid Drainage Remediation in Europe is focused on European issues associated with abandoned mines and acid drainage. European acidic drainage occurs in areas ranging from the high Arctic to circum-Mediterranean deserts.

http://www.padre.imwa.info/

PMA

The Post-Mining Alliance was developed to network, facilitate communication, and implement changes to redevelop abandoned and idle mine properties to new uses, creating new opportunities for the community. The PMA works with mine partners, regulatory agencies, and communities to find solutions for specific mining sites. The Eden Project in Cornwall, England is an example of successful postmining regeneration.

http://www.postmining.org/

SURF

The Sustainable Remediation Forum promotes the use of sustainable practices during the implementation of remedial action activities, with the objective of balancing economic viability, conservation of natural resources and biodiversity, and enhancement of the quality of life in surrounding communities. Mine reclamation fits well into the SURF mission.

http://www.sustainableremediation.org/

APPENDIX B
ACRONYMS USED IN ACID DRAINAGE LITERATURE

µg/L	micrograms per liter
1D, 2D, 3D	one-, two-, three-dimensional
A&C	abatement and control
A&I	alternative and innovative (wastewater treatment system)
AAEE	American Academy of Environmental Engineers
AAPP	Arizona aquifer protection permit
AARC	Alliance for Acid Rain Control
AAS	atomic absorption spectroscopy
AASS	actual acid sulfate soils
ABA	acid–base accounting
ABEL	US EPA's computer model for analyzing a violator's ability to pay a civil penalty
ABES	Alliance for Balanced Environmental Solutions
AC	actual commitment; advisory circular
ACA	American Conservation Association
ACE	U.S. Army Corps of Engineers; any credible evidence
ACFM	actual cubic feet per minute
ACL	alternative concentration limit; analytical chemistry laboratory
ACMER	Australian Centre for Minerals Extension and Research
ACQR	air quality control region
ACQUIRE	aquatic information retrieval
ACT	American Chemical Society; annual commitment system action
ACWA	American Clean Water Association
AD	acid drainage
ADABA	acceptable database
ADB	applications database
ADEQ	Arizona Department of Environmental Quality
ADI	acceptable daily intake
ADQ	audits of data quality
ADR	alternative dispute resolution
ADTI	Acid Drainage Technology Initiative
AFA	American Forestry Association
AFCEE	Air Force Center for Environmental Excellence

AG	acid generating
Ag	silver
AGP	acid-generating potential
AIT	alkaline injection technology
Al	aluminum
ALD	anoxic limestone drain
AMD	acid mine drainage
ANC	acid-neutralizing capacity
ANP	acid-neutralizing potential
ANSTO	Australian Nuclear Science and Technology Organization
AP	acid production (or generating) potential
APS	alkalinity-producing system
ARAR	applicable or relevant and appropriate requirement
ARD	acid rock drainage
As	arsenic
ASS	acid sulfate soils
ASTM	American Society for Testing and Materials
Au	gold
AVIRIS	Airborne Visual and Infra-red Imaging Spectrometer
AVS	acid-volatile sulfide
B	boron
BADCT	best available demonstrated control technology
BAT	best available technology
BC	British Columbia
BC SWEP	British Columbia special waste extraction procedure and modification
BCR	biochemical reactor
BCRC	British Columbia Research confirmation test
BCRI	British Columbia Research initial test
Be	beryllium
bgs	below the ground surface
BIA	Bureau of Indian Affairs
BLM	biotic ligand model; U.S. Bureau of Land Management
BMP	best management practices
BOD	biochemical oxygen demand
BP	before present
°C	degrees Celsius

Ca	calcium
CA WET	California waste extraction test
CASRN	Chemical Abstracts Services Registry Number
CBI	confidential business information
Cd	cadmium
CEQ	Council on Environmental Quality
CEQA	California Environmental Quality Act
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act (U.S. EPA)
CFR	*Code of Federal Regulations*
CGM	cyanobacteria–algae mat
Cl	chloride
cm	centimeter
CMC	criterion maximum concentration
CN	cyanide
Co	cobalt
COC	contaminant of concern
COD	chemical oxygen demand
COE	U.S. Army Corps of Engineers
Cr	chromium
CSM	conceptual site model
CTW	constructed treatment wetland
Cu	copper
CWA	Clean Water Act
DCC	direct capital costs
DI	deionized water
DL-SX	dump leach solvent extraction
DO	dissolved oxygen
DOD	dissolved oxygen demand
DOE	U.S. Department of Energy
DQO	data quality objectives
EA	environmental assessment
EA/EIR	environmental assessment/environmental impact report
ECHO	EPA's Enforcement History and Online Database
EECA	engineering evaluation/cost analysis
EIR	environmental impact report
EIS	environmental impact statement

EIS/EIR	environmental impact statement/environmental impact report
EMP	environmental management plan
EMS	environmental management system
ENV	effective neutralizing value
EP toxicity	extraction procedure toxicity test
EPA	U.S. Environmental Protection Agency
eq/ton	equivalents of calcium carbonate per ton
ERA	environmental risk assessment
ETSC	U.S. EPA Engineering Technical Support Center
F	flotation; fluorine
FBC	fluidized-bed combustion
Fe	iron
FG	flotation and gravity
FLT	fluid leaching test
FOIA	Freedom of Information Act
FONSI	finding of no significant impact
FS	feasibility study
ft	feet
g/L	grams per liter
GCL	geosynthetic clay liner
GIS	geographic information system
g	gram
gal/min	gallons per minute
ha	hectare
HCT	humidity cell test
HDPE	high-density polyethylene
HDS	high-density sludge
Hg	mercury
HHRA	human health risk assessment
HL	heap leach
h	hour
IC	indirect cost
ICARD	International Conference on Acid Rock Drainage
ICMM	International Council on Mining and Metals
ICP-MS	inductively coupled plasma mass spectroscopy
IGWMC	International Groundwater Modeling Center

INAP	International Network for Acid Prevention
ISO	International Standards Organization
ITRC	Interstate Technology and Regulatory Council
K_d	distribution coefficient
kg	kilogram
L	liter
LAD	land application discharge
LBOS	limestone-buffered organic substrate
lb	pound
LOE	line of evidence
LOS	limestone/oscillatoria
m	meter
M	molar
m/m	management and maintenance
M^{2+}	divalent metalsspacer
MAS/MILS	Mineral Availability System/Mineral Industry Locater System
MCL	maximum contaminant level
MCL/SMCL	maximum contaminant level/secondary maximum contaminant level
MDEQ	Montana Department of Environmental Quality
MEND	mine environmental neutral drainage
MEP	multiple extraction procedure
MEPA	Montana Environmental Protection Act
Mg	magnesium
mg/L	milligrams per liter
min	minute
MIW	mine-impacted water (mine-influenced water)
mL	milliliter
ML	metal leaching
MLSS	mixed liquor suspended solids
MLVSS	mixed liquor volatile suspended solids
mm	millimeter
MMB	microbial mat bioreactor
Mmol	mileimole
Mn	manganese
MP	management plan
msl	mean sea level

MWMP	meteoric water mobility procedure
N	normal; nitrogen
NAA	neutron activation analysis
NAG	net acid generating
NAPP	net acid-producing potential
NCV	net carbonate value
NDEP	Nevada Division of Environmental Protection
NEPA	National Environmental Policy Act
NF	nanofiltration
NGO	nongovernmental organization
NH_4	ammonia
Ni	nickel
NMA	National Mining Association
NMD	neutral mine drainage
NNP	net neutralizing potential
NO_3	nitrate
NOAA	National Oceanic and Atmospheric Administration
NP	neutralizing potential
NP/AP	neutralizing potential/acid potential
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
NPS	National Park Service
NPV	net present value
NRC	National Research Council
O&M	operation and maintenance
O/M	operation/maintenance
OD	outside diameter
OMB	Office of Management and Budget
OP	open pit
OPPTS	Office of Prevention of Pesticides and Toxic Substances
ORD	Office of Research and Development
ORP	oxygen-producing material
OSC	on-site coordinator; on-scene coordinator
OSHA	Occupational Safety and Health Act
OSM	U.S. Office of Surface Mining
OSW	Office of Solid Waste

OSWER	Office of Solid Waste and Emergency Response
OU	operable unit
OW	Office of Water
P	pressure; phosphorus
PAG	potentially acid generating
PAH	polyaromatic hydrocarbon
PASS	potential acid sulfate soil
Pb	lead
PCB	polychlorinated biphenol
PE	polyethylene
PER	preliminary environmental review
PGM	platinum group mineral
PGOS	pea gravel/oscillatoria
pH_F	field pH (pH of soil and deionized water)
pH_{FOX}	field pH (pH of soil and hydrogen peroxide)
pH_{KCl}	pH of a 1 : 5 solution of soil and 1 M KCl
PIRAMID	passive in situ remediation of acidic mine/industrial drainage
PLS	pregnant leach solution
POCAS	peroxide oxidation combined acidity and sulfate method
POTW	publicly owned treatment works
ppm	parts per million
PRB	permeable reactive barrier
PRG	preliminary remediation goal
PRP	potentially responsible party
PRZ	permeable reactive zone
PTS	passive treatment system
PVC	poly(vinyl chloride)
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
RAGS	Risk Assessment Guidance for Superfund
RAMS	restoration of abandoned mine sites
RAO	remedial action objective
RAPS	reducing alkalinity-producing system
RCRA	Resource Conservation and Recovery Act (U.S. EPA)
redox	reduction–oxidation

RFA	RCRA facility assessment
RFI	RCRA facility investigation
RFS	RCRA facility study
RI/FS	remedial investigation and feasibility study
RO	reverse osmosis
ROD	record of decision
RPM	remedial project manager
RWD	report of waste discharge
RWQCB	Regional Water Quality Control Board (California)
S	smelter; sulfur
SACM	Superfund accelerated cleanup model
SAP	sample and analysis plan
SAPS	sequential alkalinity-producing wetlands
SARA	Superfund Amendments and Reauthorization Act (U.S. EPA)
Sb	antimony
SC	specific conductance
S_{CR}	chromium-reducible sulfur
SDWA	Safe Drinking Water Act
Se	selenium
SEIS	supplemental environmental impact statement
SEM	scanning electron microscope
SEM/EDS	scanning electron microscopy/energy dispersive system
SITE	superfund innovative technology evaluation
SLS	sodium lauryl sulfate
SMCRA	Solid Mining Control and Reclamation Act
SME	Society of Mining, Metallurgy, and Exploration
SO_4	sulfate
SOD	soil (or solid) oxidant demand
SOP	standard operating procedure
SPLC	
SPLP	synthetic precipitation leaching procedure
SPOCAS	suspended peroxide oxidation combined acidity and sulfate method
S^{POS}%	Peroxide oxidizable sulfur
spp.	plural of *species*
SRB	sulfate-reducing bacteria

ssp.	subspecies
SSRE	sequential saturated rolling extraction
STLC	soluble threshold limit concentration
SVOC	semivolatile organic compound
SWCB	state water control board
SX/EW	solvent extraction electrowinning
T	temperature
tons/kton	tons per kiloton
TAA	total actual acidity
TAG	technical assistance grant
TCA	total potential acidity
TCLP	toxicity characteristics leaching procedure
TDS	total dissolved solids
TF	trickling filter
TIC	total inorganic carbon
Tl	thallium
TMDL	total maximum daily limit; total maximum daily load
TOC	total organic carbon
TOD	total oxygen demand
TOS	total oxidizable sulfur
TOSC	technical outreach services for communities
TRW	technical review workgroup
TSA	total sulfidic acidity
TSCA	Toxic Substances Control Act
TSF	tailings storage facility
TTLC	total threshold limit concentration
U	uranium
UG	underground
UIC	underground injection control
UNEP	United Nations Environmental Program
U.S.	United States
U.S. EPA	U.S. Environmental Protection Agency
USACOE	U.S. Army Corps of Engineers
USCG	U.S. Coast Guard
USDA	U.S. Department of Agriculture

USDI	U.S. Department of the Interior
USEPA	U.S. Environmental Protection Agency
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
VFA	volatile fatty acid
VL	vat leach
VMS	volcanic massive sulfide
VOC	volatile organic compound
WAD	weak acid dissociable
WET	California waste extraction test
WGA	Western Governors' Association
WQ	water quality
WWG	World Wide Acid Rock Drainage Guide
XRD	x-ray diffraction
XRF	x-ray fluorescence
Zn	zinc
ZVI	zero-valent iron

Reference

U.S. Environmental Protection Agency; http://www.epa.gov/aml/gloss.htm.

APPENDIX C
GLOSSARY OF ACID DRAINAGE AND MINING TECHNICAL TERMS

Acid-base accounting

A general term referring to the quantification of acid generating potential and acid neutralization potential by static testing.

Acid general potential (AGP)

The amount of acid that can be generated by weathering of minerals in a rock without considering *Acid Neutralization Potential*. The AGP is measured by static acid-base accounting procedures and is usually expressed in calcium carbonate equivalence (e.g., tons CaCO per kiloton of materials). AGP must be considered in conjunction with *Acid Neutralization Potential* to determine the net potential for production of acid.

Acid mine drainage (AMD)

A condition of surface runoff or infiltration of water with low pH and elevated concentrations of dissolved natural constituents (e.g., metal salts) resulting from weathering of certain rock-forming minerals. Both a source of acid generation and a supply of water adequate for transport of the acid must be present for this phenomena to occur. AMD may be most frequently attributed to mining sites (thus the term Acid “Mine” Drainage), but can occur from any area where there is adequate water in contact with unoxidized (i.e., sulfide) rock that has been excavated and moved to a location where oxidation is rapid compared to its natural state. A term sometimes used as a synonym is *acid rock drainage*.

Acid neutralization potential (ANP)

The amount of acid that can be consumed by minerals in a rock or soil. The ANP is measured by static acid-base accounting procedures and is usually expressed in calcium carbonate equivalence.

Active fault

an *Active Fault* is a fault that has experienced rupture in the past 35,000 years.

Adsorption

A chemical process where a molecule attaches to the surface of another phase, without becoming incorporated into that phase.

Alluvium

A general term for unconsolidated geologic materials deposited by running water (e.g., streams and rivers).

Anoxic limestone drain

A seepage treatment system comprised of a crushed limestone filled french drain designed to result in through flow under oxygen deficient (reducing) conditions to remove metals and acidity.

Anticline

A geologic structure consisting of a fold in which rock strata decrease in age away from the core of the fold. (i.e., an arch-shaped fold unless the structure has been overturned).

Aquifer

A geologic unit that contains sufficient saturated permeable material to yield usable quantities of water to a well or spring.

Aquifer loading

The quantity of a potential pollutant or pollutants able to migrate downward to the uppermost aquifer underlying a facility or site, usually expressed in mass per unit area per unit time.

Aquitard

A natural zone of low permeability that inhibits the migration of groundwater.

Attenuation (Natural)

The process by which a compound is reduced in concentration over time, through adsorption, degradation, dilution, and/or transformation.

Atterberg limits

Water content boundaries between the states of consistency of a soil (e.g., plastic limit).

Barren solution

Solution applied to ore to dissolve mineral commodities. Leaching operations in arid climates such as Nevada are usually a closed-loop recirculating system, where the barren solution is reconstituted from pregnant solution after processing, with make-up water added as necessary.

Batch test

A test involving reacting or leaching a quantity of representative material (e.g., soil ore, tailing) to obtain empirical data.

Beach

The sloping surface of hydraulically deposited tailing material.

Bedrock

A general term for consolidated and lithified geologic materials.

Borrow

Earth materials used for construction.

Bulk density

The density of a material measured in mass per unit volume.

Buttress

An engineered structure and/or compacted earth support system for stabilizing over steepened slopes at their toe.

Column test

A test designed to simulate the leaching or reaction of a liquid percolated through a granular material (e.g., soil, ore, tailing). The granular material is normally contained in a vertical pipe or column, with

liquid added at the top and effluent collected at the bottom.

Composite liner

A liner comprised of two or more low permeability components in direct contact with each other (e.g., a layer of clay and a geomembrance).

Cone of depression

The depression produced in a water table or piezometric surface by pumping.

Design earthquake

An earthquake utilized as the basis for developing appropriate ground motion characteristics for seismic design of a facility.

Design peak flow

The maximum flow rate calculated for the design storm at a given point in an engineered drainage system. Design peak flow is used in sizing components that convey flow (e.g., ditches and channels)

Design storm

The storm size (usually identified by recurrence interval and duration) utilized in the design and sizing of engineered drainage systems.

Design storm volume

The total runoff volume that discharges to an engineered pond or impoundment during the design storm.

Detoxification

The treating of spent ore or other mine waste to reduce or eliminate its toxicity. Detoxification procedures can include rinsing and physical, chemical or biological treatment.

Discharge

The addition of a pollutant from a facility either directly to an aquifer or to the land surface or the vadose zone in such a manner that there is reasonable probability that the pollutant will reach an aquifer.

Dry unit weight

The weight of mineral matter divided by the volume of the entire element. Also referred to as dry density.

Ecological survey

for the purposes of this IM, Ecological Survey means inventorying wildlife, vegetation, and wildlife habitat within a defined area proposed for a specific activity, such as a land application.

End dumping

The process of dumping material from the back of a dump truck. Dump leach piles, heap leach piles and overburden rock piles are commonly constructed by end-dumping the material over the top edge of the pile slope.

Evaporative depth

The depth below the ground surface to which water can be removed through evapotranspiration.

Factor of safety

The ratio of forces contributing to slope stability (e.g., due to intergranular friction and cohesion) versus forces working against slope stability (e.g., gravity, seismic acceleration) estimated in seismic stability analyses.

Fixation

A process by which chemical constituents are immobilized or chemically bound in a matrix.

Freeboard

Height of containment above the surface of a contained liquid.

Gabion

A cylinder or cage, usually constructed of metal mesh, filled with rocks and used for erosion protection in storm water control channels, at dam foundations, etc.

Geocomposite

A general term for a premanufactured composite material (e.g., geosynthetic clay liner) designed for use in engineered structures.

Geomembrance

A low permeability plastic liner.

Geonet

A coarse plastic net designed for use as a drainage layer in engineered systems.

Geosynthetic

A general term for synthetic materials (e.g., geomembranes or geotextiles) used in engineered earth structures.

Geosynthetic-clay liner (GCL)

A factory-manufactured hydraulic barrier typically consisting of bentonite clay or other very low permeability material supported by geotextiles or geomembranes which are held together by needling, stitching or chemical adhesives.

Geotextile

A fabric designed for various uses in engineered earth structures. Common uses include wrapping or covering of materials to be buried to prevent their physical damage, incorporation into fills to spread load distribution, and use as a filter medium to capture fine particles.

Head or hydraulic head

The height of a fluid above a reference point (e.g., a plastic liner). Head is the driving force that exerts pressure causing water to migrate.

Heap leach pad

A lined relatively flat constructed area and solution containment features, on which ore is loaded and then leached with a solution to dissolve and recover minerals.

Hydraulic conductivity

A measurement of the relative ease with which a porous medium can transmit water under a potential gradient. It is dependent on physical properties of the porous medium (i.e., the size, shape and degree of connection between openings through which liquid can flow).

Hydrograph

A water level or rate of flow record as a function of time.

Hydrolysis

Decomposition or alternation of a chemical substance by water.

Infiltration

Downward movement of water through the soil surface into the ground. Some or all of the water than infiltrates may still be removed through evapotranspiration.

Injection well

A well which receives discharge through pressure injection or gravity flow. Injection wells are commonly used to deliver leaching solution to an ore body for insitu leaching operations.

In-situ leaching

The application of leaching solution to an ore body that is in-place, for the purpose of extracting a mineral commodity.

Interface strength

The shear strength at the interface of two materials (e.g., the contact between a plastic liner and a clay layer).

Invert

The low point of drainage collection or conveyance system.

Kinetic acid-base analysis

Laboratory tests designed to initiate what happens in nature and run over a period of time to determine the potential for rock to be acid-generating. Kinetic testing methods include humidity cell tests, column tests, etc.

Leaching

The process of dissolving mineral commodities from ore. For copper ores, leaching is usually accomplished by treating the ore with and acidic solution. For precious metals ores, leaching is usually accomplished using a basic solution with additional reagents to dissolve the mineral commodity (e.g., sodium cyanide).

Lithology

The physical and mineralogical makeup of geologic materials.

Liquefaction

The sudden large decrease of shearing resistance of cohesionless soil caused by a collapse of the structure by shock or strain (such as an earthquake) and associated with an increase of pore water pressure.

Lixiviant

A fluid used for leaching or extracting mineral or other components from solid material.

Lysimeter

A device used to measure the quantity or rate of movement of water through soil, or to collect such water.

Maximum credible earthquake (MCE)

The maximum earthquake that appears capable of occurring based on the presently known tectonic framework.

Maximum probable earthquake (MPE)

The maximum earthquake likely to occur during a 100-year interval (80 percent probability of not being exceeded in 100 years).

Mine pit

An area from which ore and overburden are excavated.

Non-storm water pont

A pond that contains seepage or inflow from a tailing impoundment, waste dump, process area, etc., where potential pollutant constituents in the seepage or inflow have concentrations that are relatively low (e.g., compared to process solutions) but exceed Arizona surface water quality standards. Non-storm water ponds also include secondary containment structures and overflow ponds that contain process solution for short periods of time due to process upsets or rainfall events.

Optimum moisture content

The moisture content at which the greatest degree of compaction is obtained.

Ore

Rock that can be mined for extraction of a minerals commodity under conditions that allow a profit to be made.

Outcrop

A bedrock exposure at the ground surface.

Overburden

Non-Ore rock and soil overlying an ore body. Non-ore rock that is interspersed with ore is also often referred to as overburden. For surface mining operations, overburden must usually be excavated to access ore material for removal. Mining operations characteristically minimize the amount of overburden excavated to control mining costs. Overburden is also referred to as *waste rock*.

Oxidation

Any process which increases the proportion of oxygen or acid-forming or radical in a compound.

Oxide ore

Ore material that has been oxidized through natural geologic processes and no longer contains significant quantities of sulfide minerals.

Packer

A tool used to seal a well or boring at a specific location to isolate a given vertical zone (e.g., for testing or production).

Passive containment

Natural or engineered topographical, geological or hydrological control measures that can operate without continuous maintenance.

Peak flow

The maximum flow rate for a given storm at a given point in an engineered drainage system.

Perched water table

The top surface of a local zone of saturation located above the regional water table. Perched water table usually occur immediately above a low permeability stratum within the vadose zone that intercepts downward-percolating water and causes some of it to accumulate above the stratum.

Percolation

Downward movement of water is the vadose zone. Percolation occurs when the moisture content exceeds the specific retention.

Permeability

A measurement of the relative ease with which a porous medium can transmit liquid under a potential gradient. It is dependent on physical properties of the liquid (i.e., viscosity and density) and the porous medium (i.e., the size, shape and degree of connection between openings through which liquid can flow).

Phreatic surface

The water table or top surface of a zone saturated with water with an engineered earthen structure (e.g., an embankment).

Pore pressure

Pressure present within the pore fluid of a soil.

Porosity

The percentage of the total volume of rock or soil that is occupied by void space.

Pseudo static analysis

State analysis of slope stability that incorporates a simulated horizontal force equal to the horizontal acceleration of the design earthquake times the mass of the potentially sliding material.

Pregnant Solution or Pregnant Leach Solution (PLS)

Mineral-laden solution recovered from a leaching operation. Leaching operations in arid climates such as Nevada are usually a closed-loop recirculation system, where the mineral commodity of interest is recovered from the pregnant solution and residual liquid is refortified with leaching reagent to make barren solution.

Process solution pond

A pond that contains pregnant, barren or recycling process solutions. An overflow pond that

continually contains process solution as a normal function of facility operations is also considered a process solution pond.

Quality assurance

A planned system of activities that provide assurance that a facility was constructed as specified in the design.

Quality control

A planned system of inspections that are used to directly monitor and control the quality of a construction project.

Raveling

Rolling of loose surficial rocks down a slope due to gravity.

Recovery well

A well utilized to recover mineral-laden solution as part of an in-situ leaching process.

Riprap

Rock placed in channels, on embankments, etc. to prevent erosion.

Risk assessment

An organized process used to describe and estimate the likihood of an adverse exposure to toxic constituents in soil, water, and air.

Risk management

Risk Management is a practice with processes, methods, and tools for managing risk in a project or action. It provides a disciplined environment for proactive decision making to assess risk, determine which risks are important to deal with, and implement strategies to deal with those risks.

Rubbilization

The engineered blasting of in-place rock to increase its permeability for the purpose of facilitating in-situ leaching.

Run of mine

Uncrushed rock, broken only by blasting and excavation.

Run-on

Surface flow onto or into a given area caused by precipitation.

Run off

Surface flow from a given area caused by precipitation that does not infiltrate or evaporate.

Run-out

Transport of soil or rock beyond the toe of a slope due to momentum from dumping from the top of the slope.

Seismicity

Movement of the ground caused by an earthquake.

Settlement

The gradual downward movement of a structure due to loading and compression of the soil below the foundation.

Sliding block failure

A form of landslide movement in which an entire large block of materials, typically rock, moves as a unit for some distance out of a slope.

Slime sealing

The hydraulic placement of finely ground tailing in a manner designed to create a hydraulic barrier/layer (e.g., against the up gradient side of a tailing impoundment embankment).

Specific retention

Ration of the volume of water a soil or rock can retain against gravity drainage to the total volume of the soil or rock.

Static water elevation

The equilibrium elevation of standing water in a well or piezometer not affected by pumping.

Static stability

The relative stability of a slope or structure under static (non-seismic) conditions.

Sub aerial deposition

The hydraulic deposition of tailing in thin layers for defined periods of time over a beach in a manner that promotes rapid dewatering and evaporative drying of the deposited tailing.

Subsidence

Mass movement involving gradual downward sinking of the ground surface.

Sulfide ore

Ore material that contains significant quantities of sulfide minerals.

Surface pond

An impoundment other than a tailing impoundment that is used to collect or store fluids at a mining operation.

Syncline

A geologic structure consisting of a fold in which rock strata increase in age away from the core of the fold. (i.e., a trough-shaped fold unless the structure has been overturned).

Tailing

Finely ground ore residue remaining after milling and mineral extraction.

Tailing impoundment

An impoundment designed to receive and contain finely ground ore residue particles and residual leach or chemical solutions remaining after milling and minerals extraction.

Talus

Unconsolidated rock or soil fragments deposited at the base of slopes due to gravity.

Unnecessary and undue degradation

Means conditions, activities, or practices that: (1) Fail to comply with one or more of the following: the performance standards in 43CFR 3809.420, the terms and conditions of an approved plan of operations, operations described in a complete notice, and other Federal and state laws related to environmental protection and protection of cultural resources;(2) Are not “reasonably incident” to prospecting, mining, or processing operations as defined in 43CFR 3715.0-5 of this chapter; or(3) Fail to attain a stated level of protection or reclamation required by specific laws in areas such as the California Desert Conservation Area, Wild and Scenic Rivers, BLM-administered portions of the National Wilderness System, and BLM-administered National Monuments and National conservation Areas.

Vadose zone

A zone below the ground surface containing water under pressure that is less than atmospheric pressure. Also referred to as the *unsaturated zone*.

Waste rock

See Overburden.

Water balance

The net sum of liquid inflows and outflows for a given system.

Watershed

The area that contributes surface runoff to a given system.

References

U.S. Bureau of Land Management. http://www.blm.gov/pgdata/ etc/medialib/blm/nv/minerals/mining.Par.19143.File.dat/ Glossary%20of%20Technical%20Terms.pdf.

Other Public Domain Glossaries

U.S. Environmental Protection Agency. http://www.epa.gov/ aml/gloss.htm. http://www.epa.gov/superfund/policy/remedy/ pdfs/appendix.pdf.

U.S. Department of Agriculture. http://www.nrcs.usda.gov/ Internet/FSE_PLANTMATERIALS/publications/azpmctn10801 .pdf.

U.S. Geological Survey. http://energy.usgs.gov/GeneralInfo/ HelpfulResources/EnergyGlossary.aspx.

APPENDIX D
CHEMICAL EQUILIBRIUM DIAGRAMS

The U.S. Geological Survey has prepared numerous reports and chemical equilibrium diagrams for groundwater systems (Hem, 1). The chemical composition of natural water is derived from many different sources of solutes, including gases and aerosols from the atmosphere, weathering and erosion of rocks and soil, solution or precipitation reactions occurring below the land surface, and cultural effects resulting from human activities. Broad interrelationships among these processes and their effects can be discerned by application of the principles of chemical thermodynamics. Some of the processes of solution or precipitation of minerals can be closely evaluated by means of the principles of chemical equilibrium, including the law of mass action and the Nernst equation (Hem, 1985). Figure D.1 is a chemical equilibrium diagram for sulfur, a part of the original iron sulfide, as well as the source of sulfur for the sulfate and sulfuric acid. Figures D.2 and D.3 are chemical equilibrium diagrams for iron, which is a part of the iron sulfide source material for acid drainage and frequently a metal that becomes released into the acid drainage solution as the pyrite source material dissolves under oxidizing conditions. Figure D.4 is a chemical equilibrium diagram for aluminum, representing a common metal contaminant associated with acid drainage and released into the environment.

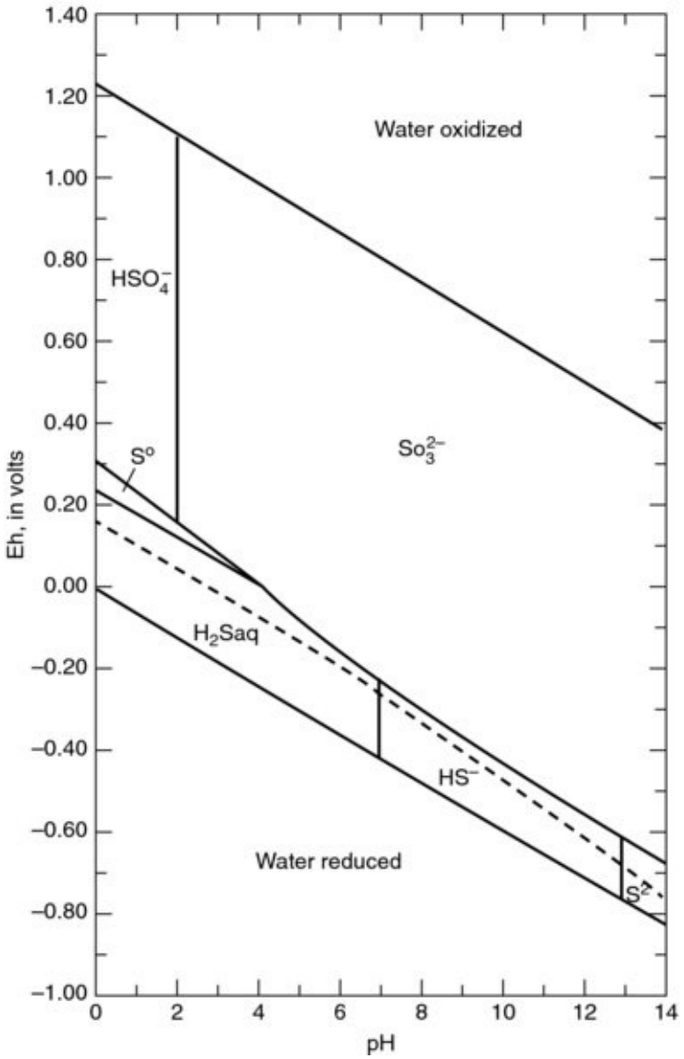


FIGURE D.1 Fields of dominance of sulfur species at equilibrium at 25°C and 1 atm pressure. Total dissolved sulfur activity at 96 mg/L as SO_4^{2-}. The dashed line represents redox equilibrium between dissolved CO_2 species and methane (CH_4). (From Hem, 1.)

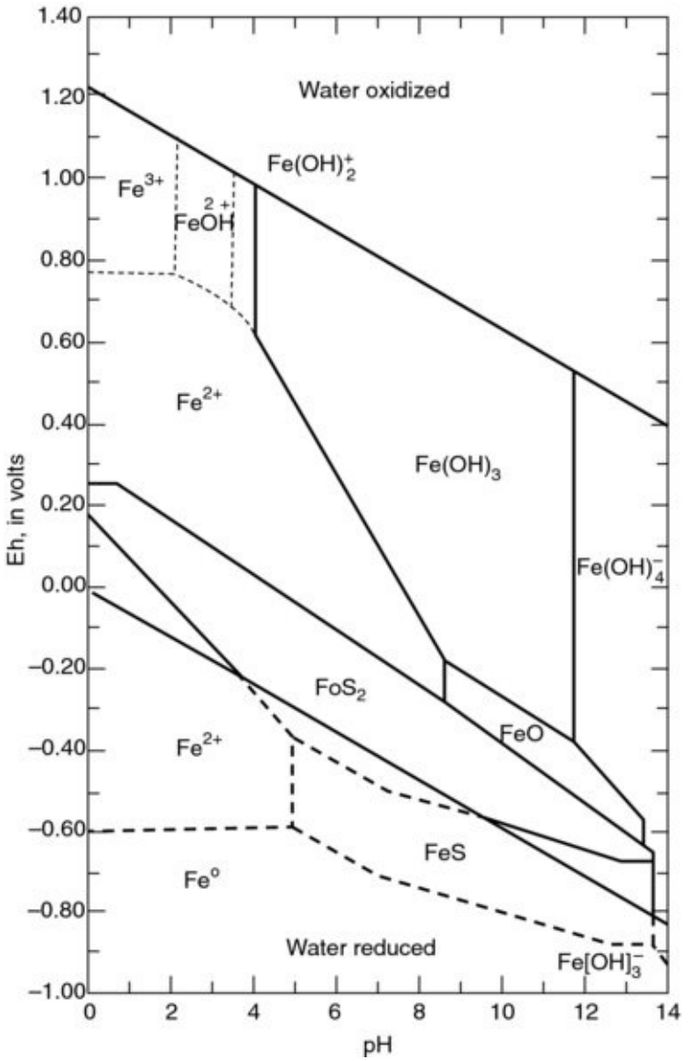


FIGURE D.2 Fields of stability for solid and dissolved forms of iron as a function of Eh and pH at 25°C and 1 atm pressure. Activity of sulfur species 96 mg/L as SO_4^{2-}, CO_2 species 61 mg/L as HCO_3^-, and as dissolved iron 56 g/L. (From Hem, 1.)

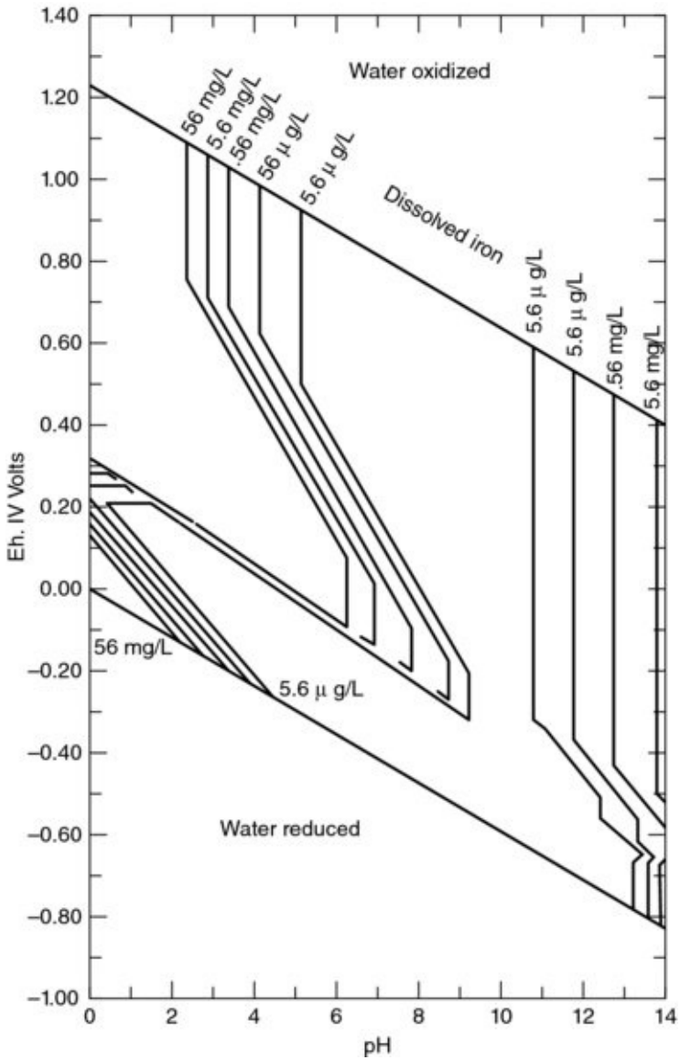


FIGURE D.3 Fields of stability for solid and dissolved forms of iron as a function of Eh and pH at 25°C and 1 atm pressure. Activity of sulfur species 96 mg/L as SO_4^{2-}, CO_2 species 61 mg/L as HCO_3. (From Hem, 1.)

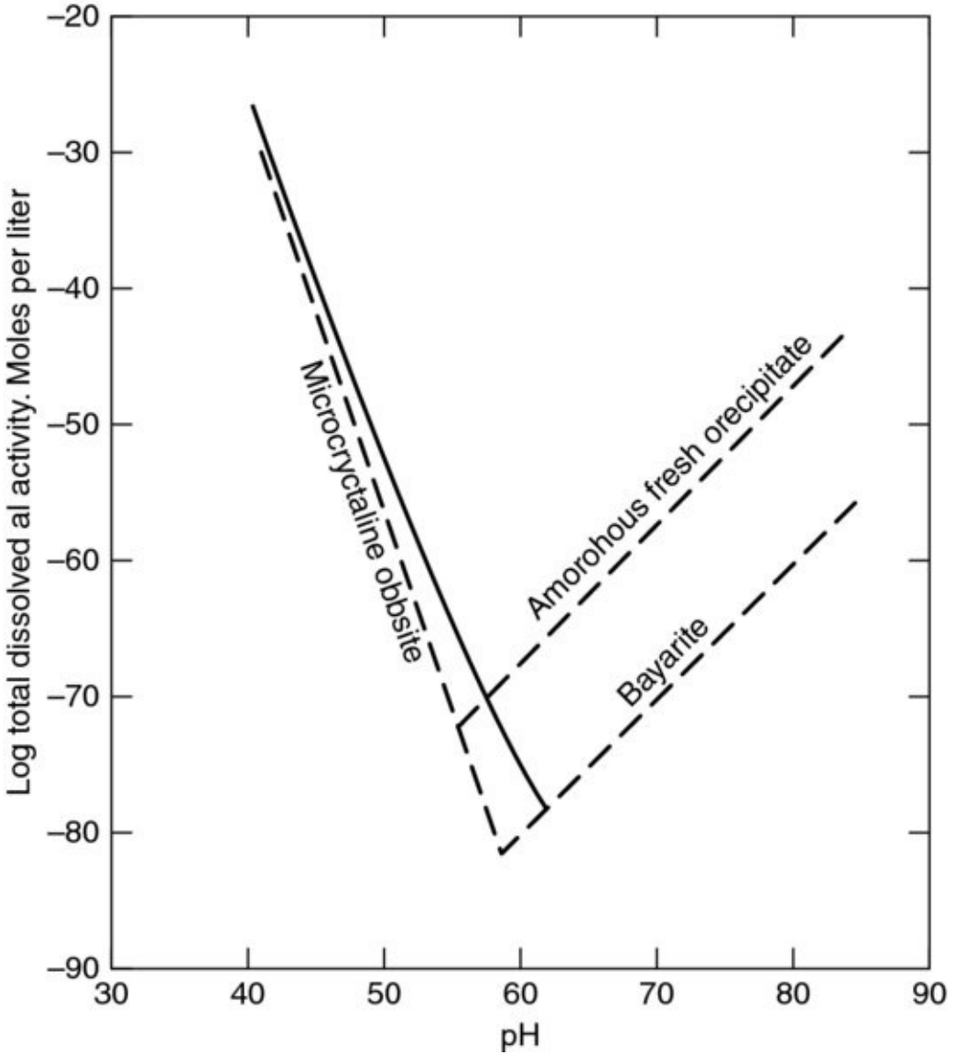


FIGURE D.4 Equilibrium activities of free aluminum for three forms of aluminum hydroxide (dashed lines) and calculated activity of Al^{3+} and $AlOH^{2+}$ (solid line). (From Hem, 1.)

Reference

Hem, J.D., 1985. Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd ed. Water-Supply Paper 2254. U.S. Geological Survey, Reston, VA. 263 pp.

APPENDIX E
SOIL AND GROUNDWATER SAMPLING METHODS FOR ACID DRAINAGE STUDIES

JAMES A. JACOBS

For environmental soil sampling projects, clear acetate, stainless steel, and brass liners are commonly used with most sampling tools, including the tools described below. Handheld or portable electric, hydraulic, or pneumatic rotohammers or jackhammers can be added to the manual sampling system to extend the sampling depth. Reversing the direction of hammering on the slide hammer can provide enough force to extract the sampler and rods. As the depth of sampling increases, the side friction on the samplers and possibly sampling extension rods increases. For removal of the samplers at greater depth, manual probe rod jacks supply approximately 2000 to 4500 lb of lift capacity needed for soil or groundwater sampler extraction. Handheld soil-sampling equipment can be used to perform sampling at an angle as well as horizontal sampling. For shallow simple acid sulfate soil investigations, acid mine drainage in areas with small waste rock diameter (less than 1 in. in diameter), or shallow construction projects, manual samplers and cone penetrometer testing or direct-push technology rigs are likely to work well.

Cone Penetrometer Testing Method

Direct-push technology (DPT) samplers and rigs can be used for acid generation studies at mine sites and construction projects, and for investigating acid sulfate soils. DPT, also called *drive point sampling*, is a technique that uses soil or groundwater samplers that are driven into the subsurface without the rotary action and production of drill cuttings associated with hollow-stem auger rigs. DPT, including cone penetrometer testing (CPT) rigs, use the static weight of the vehicle to push the sampling rods into the ground. CPT rigs use a 20-ton truck and are capable of sampling in soils to depths of 250 ft. CPT rigs, originally developed for use in the geotechnical field, typically push from the center of the truck.

The typical CPT rig is used to hydraulically push into the subsurface small-diameter [1.6 in. according to American Society of Testing and Materials (ASTM) specifications] instrumented probe and steel support rods. The pushing generally occurs from the center of the truck; consequently, angle borings are generally not carried out with a CPT rig. Variations in probe dimensions are becoming more commonplace, depending on the particular application. The conventional probes used with the hydraulic ram systems are equipped with transducers for measuring point penetration resistance and sleeve friction. An empirical relationship between these physical strength measurements and soil types is used to derive soil classification logs for the layers penetrated. Not surprisingly, these conventional types of probes have been used extensively by geotechnical engineers in the construction industry. Although originally designed for geotechnical subsurface investigations, CPT rigs have been used more frequently for environmental applications (Kram and Lieberman, 2000).

In addition to the conventional soil classification devices mentioned above, probes have recently been developed to meet the requirements of environmental professionals tasked with characterizing site hydrogeological and contaminant characteristics. For hydrogeological purposes, sensor probes have been developed to determine soil type, vadose zone moisture content, water table elevation, groundwater flow rate, aquifer communication areas, and the distribution of hydraulic conductivity. Many sample collection

options exist for CPT rigs, each depending on the specific medium. Many CPT soil samplers resemble their hollow-stem drill counterparts in that a split-spoon cutting tool is used for collection. Typically, a push rod with a closed tip (piston sampler) is advanced to a depth just above the sampling depth desired. The cutting tip of a CPT sampler is generally opened using a spring-loaded hinge system inside the sampling string. Once the hinge is triggered, the open cutting tube is advanced to the depth desired, filling the cylindrical sample chamber with soil. The former tip is retracted during collection. This technique tends to work best in dry soil with low gravel percentages. In some overpressured sandy environments beneath the water table, sample collection can be difficult. If relatively finer-grained material is located below the sand of interest, it is sometimes useful to space the sampling interval so that the finer material forms a plug at the bottom of the push stroke.

CPT groundwater samplers typically work by either pumping or mass displacement. CPT groundwater samples commonly use the ConeSipper water sampler, which consists of a screened lower chamber and an upper collection chamber. Two small-diameter Teflon tubes connect the upper collection chamber to a control panel in the truck. The truck ballast and hydraulic rams are used to push the sampler to a predetermined depth. While the probe is being advanced, nitrogen under relatively high pressure is supplied to the collection chamber via the pressure/vacuum Teflon tube to purge the collection chamber and prevent groundwater from entering the chamber before the probe reaches the depth desired. Once that depth is reached, the pressurized nitrogen is shut off, excess nitrogen pressure is removed from the 100-mL upper collection chamber, and the chamber fills with groundwater. Finally, nitrogen under relatively low pressure is supplied to the collection chamber to gently displace the water and slowly push the water to the surface through the small-diameter Teflon sampling tube. Slow sampling and low pressures are critical for sampling water containing volatile constituents. Sample collection times range from 20 min to 2 h, depending on the soil type adjacent to the sampling port. The groundwater samples are placed directly into proper sampling containers for the analyses requested. The sample containers are labeled, logged, and placed into a chilled cooler pending delivery to a regulatory-approved analytical laboratory.

Direct-Push Technology Sampling

Direct-push technology (DPT) rigs can install piezometers and 1- to 3-in.-diameter driven well points or piezometers. DPT rigs do not generate significant volumes of soils being brought to the surface, unlike rotary auger rigs, which generate large amounts of drilling-derived wastes. Coring starts at the ground surface with an open-tube soil sampler. A DPT rig can install a prepacked monitoring well point in which the soils in the borehole are pushed out of the way and flattened against the borehole walls by the probe tip as it descends. The caking of sidewalls does lower the porosity and permeability of the sediments. DPT wells generally do not have large annular spaces.

Direct-push technology soil samples are commonly collected in 2- to 5-ft-long clear acetate liners contained within an outer sampler. The plastic liners are easily cut with a knife and are transparent, for easy lithological characterization. Brass, aluminum, stainless steel, or Teflon liners are also available, depending on the sampler. After removal from the sampler, the soil liner containing the sample is immediately capped on both ends with Teflon tape, trimmed, and then capped with plastic caps. The samples are labeled and placed in individual transparent hermetically sealed sampling bags. The samples are then put in the appropriate refrigerated environment and shipped under chain-of-custody procedures to a state-certified laboratory.

Various soil samplers have been designed and manufactured by numerous companies. The main sampler types used in environmental and engineering projects include split-spoon samplers, open-tube samplers,

piston samplers, and dual-tube samplers. A *split-spoon sampler* consists of a sample barrel that can be split in two along the length of the sampler to expose soil liners. A split-spoon sampler without sample liners is useful for lithological logging where soil samples will not be collected for chemical analysis.

An *open-tube sampler* contains soil liners and has been designed for environmental sampling within the same borehole, provided that soil sloughing is minimal. Continuous coring with an open-tube sampler begins at the ground surface with an open-ended sampler. The open-tube sampler is reinserted back down the same borehole to obtain the next core. An open-tube sampler works well in stable soils such as medium- to fine- grained cohesive materials such as silty clay soils or sediments. Open-ended samplers are commonly ¾ to 2 in. in diameter and 2 to 5 ft in length. The simplicity of an open-tube sampler allows for rapid coring.

For discrete sampling in unstable soils, a *piston sampler* allows the user to drive the sampler to the sampling depth selected. A piston sampler is equipped with a piston assembly that locks into the cutting shoe and prevents soil from entering the sampler as it is driven in the existing borehole. After the sampler has reached the zone of interest, the piston is unlocked to allow the soils to push the piston as the sampler is advanced into the soil.

Dual-tube soil samplers were designed to prevent cross-contamination when sampling through perched water tables. This is especially important for acid sulfate soils, where vertical variations in sulfide content may be significant over just a few inches. A dual-tube sampler has an outer rod that is driven ahead of the inner sampler. The outer rod provides a sealed hole from which soil samples can be recovered without the risk of cross-contamination. The inner rod with sampler and outer casing are driven together to one sampling interval. The inner sampling rod is then retracted to retrieve the filled liner while the outer casing is kept in place to prevent sloughing. This procedure is then repeated to the total depth. Although slower than open-tube sampling, dual-tube sampling is especially useful when sampling through sloughing soils and sediments.

Various types of sealed water samplers are available for DPT groundwater sampling to prevent cross-contamination of groundwater samples from affected soil or groundwater higher in the section. Many DPT probe water samplers use a retractable or expendable drive point. After driving to the zone of interest, the outer casing is raised from the borehole, exposing the underlying well screen. For a nondiscrete groundwater sample, the outer casing contains openslots. The open-slotted tool is driven from the ground surface into the water table. Groundwater is collected using an inner tubing or smaller-diameter bailer inserted into the center of the open-slotted water sampler.

Groundwater Monitoring with Well points

Once the site acid generation investigation objectives have been met, small-diameter well points (0.5 to <2 in. in diameter) can be installed to monitor shallow groundwater, if needed. Direct-push technology well points are typically installed without filter packs. However, robust filter pack materials specifically designed for rapid customization of direct-push technology well points have recently become available. Direct-push technology well points or piezometers with up to about a 1.0-in. inside casing diameter can been used for groundwater sampling and to gauge groundwater elevations at acid drainage sites. Well points can be designed and installed with premade sand filter packs. The well points are sealed with bentonite and cement, like a normal monitoring well. When taking water samples for acid drainage studies, field filters are frequently used when sampling for dissolved metals to remove suspended solids or colloids from the water sample.

Other Drilling Techniques

A variety of other drilling techniques have been developed and are used in the environmental field, and some of them are applicable to acid drainage studies. The factors to determine the best drilling technique relate to accessibility, time and cost of project, sediment type (consolidated rock or unconsolidated soils), sample type (undisturbed vs. disturbed), and sample integrity. Unconsolidated deposits are drilled primarily using hollow-stem augering techniques, with an occasional use of cable-tool drilling techniques. For consolidated or semiconsolidated deposits, continuous wire-line or conventional rock coring techniques are commonly used.

Hollow-Stem Auger Drilling

Hollow-stem auger drilling has been used extensively in the environmental industry for the ease of collecting soil and water samples, which are taken through the center of the drilling auger. This method lowers the chances of cross-contamination between adjacent soils and water and soils and water higher up in the section. Other auger drilling techniques used in the environmental field include the use of labor-intensive hand augers for shallow depths and machine-operated solid-flight augers. Both of these techniques can have sample retrieval problems since samples can only be collected if the entire auger is removed prior to sampling. More detail regarding drilling techniques is provided by Driscoll (1984), Testa (1994), Sisk (1981), and the California Department of Water Resources (1981, 1990). The drilling and sampling equipment may vary slightly but is generally available worldwide. The sampling procedures and drilling equipment described are used in the United States. Local and national regulatory variations exist, and checking with local regulatory authorities is recommended to determine specific drilling and sampling procedures to follow.

Hollow-stem continuous-flight auger drilling techniques are commonly used for subsurface environmental projects. Hollow-stem augers consist of a series of continuous, interconnected hollow auger flights, usually 5 to 10 ft in length. Typical hollow-stem augers for use in the environmental field have inner diameters of 4¼ to 10¼ in. to create 2- and 4-in. diameter wells, respectively. The hollow-stem augers are pressed downward hydraulically and rotated to start drilling. Soil cuttings are rotated up the outside of the continuous flighting in the borehole annulus. A center rod with a plug and pilot bit are mounted at the bottom. The plug is designed to keep soil from entering the mouth of the lead auger while drilling. Upon reaching the sampling depth, the center rod string with plug and pilot bit attached is removed from the mouth of the auger and replaced by a soil sampler.

Soil sampling is achieved by passing a smaller-diameter drill rod into a hollow-stem auger with a soil sampler attached at the bottom. The soil sampler is lowered into the borehole through the hollow stem of the auger, and sampling or coring is started. The sampler is typically either a thin-walled or modified split-barrel sampler with stainless steel or brass sample tubes. Samples can be retrieved continuously, which is recommended for acid drainage assessments. For the environmental field, the most popular split-barrel samplers are the 2½- or 3-in.-OD samplers. It is a standard split-barrel sampler that has had its interior honed or otherwise machined to accept brass or stainless steel liners or rings. The split-barrel sampler is lined by three stainless steel or brass tubes each 6 in. in length, which can be removed from the sampler for capping and shipment to the laboratory. Reloading the sampler with liners allows continuous use of the sampler.

Conventionally, the upper 6-in. sample tube is used for lithological description and physical testing (i.e., permeability, sieve analysis, etc.), the middle sample tube is used for field screening for hydrocarbon or

solvent vapors or other constituents of concern, and the bottom sample tube is used to send to a chemical laboratory for analysis. The sampler is driven into the soil at the desired sampling interval ahead of the auger bit by using a 140-lb hammer falling freely 30 in. A standard penetration test (ASTM D1586) requires a sampler with a 2-in. outside diameter, 18 to 24 in. in length, with an inside diameter of 1½ in. and a drive shoe cutting diameter of 1⅜ in. The count to advance the sampler 1 ft is the blow count. Blow counts collected by a sampler of any other size can be useful, but they are not a standard penetration blow count that may be used to determine the consistency or soil density information. Boreholes are either grouted using a tremie pipe or converted into a monitoring well. Soil cuttings are generally not used to backfill borings in environmental projects, due to the potential for cross-contamination.

Installing Environmental Monitoring Wells

For hollow-stem auger drilling, the auger will remain in the borehole while the well casing is set, to prevent caving. The well is cased with blank and factory-slotted threaded schedule 40 poly(vinyl chloride) (PVC) pipe. The slotted PVC casing is placed from the bottom of the borehole to the top of the aquifer. The blank casing extends from the top of the slotted casing to approximately ground surface. The slots are generally 0.010 or 0.020 in. wide by 1.5 in. long, with approximately 42 slots per linear foot. Slot sizes are determined by previous well installations in the area, or by a grain-size sieve analysis. A threaded PVC cap is fastened to the bottom of the casing. Centering devices may be fastened to the casing to assure even distribution of filter material and grout within the borehole annulus. Well screens and casings are typically steam cleaned, regardless of composition prior to installation, to ensure that no machine oils or other chemicals exist on the casing surfaces.

After setting the casing within the auger, sand or gravel filter material is poured into the annulus to fill from the bottom of the boring to 1 ft above the slotted interval. The auger is withdrawn without rotation as filter material is poured into the annulus between the auger and casing, being careful to ensure that 2 or 3 ft of filter material is always in the auger. Too much filter material in the auger or rotation of the auger may cause the casing to lift. Too little filter material in the auger could allow native material to corrupt the continuity of the filter pack. One to two feet of bentonite pellets is placed above the filter material and hydrated with deionized water. The bentonite pellets are placed to prevent the grout and surface contaminants from reaching the filter material. Neat cement, a common grout for sealing environmental wells, contains approximately 5% bentonite powder. When added to the neat grout, the bentonite powder must be mixed into the mixing water prior to introduction into the cement; otherwise, the differential rates of assimilation will cause uneven hydration of the cement and consequent failure of the well seal. The grout is tremied into the annular space from the top of the bentonite plug to the surface. The grout need not be tremied if the top of the bentonite plug is less than 5 ft below the ground surface and the interval is dry. Approved grout mixtures and grouting techniques may vary depending on local conditions and regulations.

A lockable PVC cap is typically placed on the wellhead. A traffic-rated flush-mounted steel cover is installed around a wellhead located in traffic areas. A steel stove pipe is usually set over a wellhead in landscaped areas. The flush-mounted cover box or stovepipe monument contacts the grout. Grout fills the space between the monument and the sides of the borehole. The monument and grout surface seal is set at or above grade so that drainage is away from the monument. The monument lid is clearly marked “Monitoring Well”, with the well number. The monument interior should also be marked with the well number in the event that the lid is lost or misplaced.

Sampling Procedures

All information pertinent to field investigations is typically kept on daily field logs and other field documents. Field observations of surface reddish-orange staining on soils, dead vegetation, dead fish or other aquatic organisms, or obvious sulfur smell should be noted on the field forms and documented with photographs. Boring logs, water sampling data sheets, and chain-of-custody forms comprise the field documents in which all pertinent information about borehole samples and groundwater samples is recorded. The information documented includes the following minimum data:

- Investigation location
- Sample number
- Sample location, boring or well number, and/or depth
- Name of collector
- Date and time of collection
- Analyses to be performed
- Field observations
- Field measurements (pH, conductivity, water levels)
- Other data forms

Equipment Decontamination

Prior to arriving at a sampling site, all hand augering and direct-push technology sampling equipment should be cleaned with phosphate-free detergent and rinsed twice with deionized water. This procedure should also be carried out on site prior to, between, and after sampling. Hollow-stem auger drilling equipment should be steam cleaned prior to arriving on site, and between uses. Decontamination is best conducted on an impermeable surface, and all effluent is contained. The drilling equipment, including augers, is commonly placed on a rack for air drying. All other sampling equipment is typically washed with nonphosphate detergent and rinsed twice with deionized water. Water used for decontamination should be stored in labeled containers certified for hazardous material storage. The decontamination water is disposed of in an approved manner. Labels should contain the following minimum information:

- Type of material contained (e.g., decontamination water)
- Date of first accumulation
- Client's name, address of site

Instrument Calibration

The following field equipment is frequently used during the environmental site investigations and remediations during sample collection. Calibration procedures and frequency are listed in manufacturers' guidebooks.

- pH-measuring tool
- Water-level meter: water depth and total depth of well
- Multiparameter meter: pH/temperature/conductivity/ dissolved oxygen

- Oxidation–reduction potential meter for water samples
- Magnetic line locating tools to measure magnetic fields related to subsurface obstructions (when drilling in a developed area)

Sample Control and Labeling

Proper identification, preparation, packaging, handling, shipping, and storage of samples obtained in the field are the responsibility of field personnel. Samples must be readily identifiable and should be as representative as possible of in situ conditions. Each sample container is labeled at the time of collection. The label is attached to the individual sample containers. The labels should contain the following minimum information:

- Project name and number
- Date and time of collection
- Name of collector
- Sample number
- Location of sample collection, well or boring number, sample depth
- Preservation or special handling employed

Chain-of-Custody Procedures

A chain-of-custody form for each sample and container is used to track possession of the samples from the time they were collected in the field until the time they are analyzed in the laboratory. The chain-of-custody form will contain the following minimum information:

- Project name and number
- Name and signature of collector
- Date and time of sample collection
- Number of containers in a sample set
- Description of sample and container(s)
- Names and signatures of persons who are involved in the chain of custody
- Inclusive dates and times of possession
- Type of analysis requested

If a sample is known to have a high chemical concentration, field personnel should make a note on the chain-of-custody from so that dilutions may be made in the laboratory.

Sample Preparation, Packaging, and Handling

Soil samples are collected in polyethylene, brass, or stainless steel sample tubes. The tube ends are covered with Teflon tape and plastic end caps, labeled, and sealed in locking plastic bags. Certain soil samples may be collected in laboratory-supplied 8-oz wide-mouth jars with Teflon-lined screw-on lids.

Groundwater samples are placed in laboratory-supplied containers that are compatible with the requested analysis. Samples are placed into a cooler containing chemical ice. Padding (i.e., bubble wrap, foam) is used to prevent glass breakage.

Sample Delivery to Laboratory

The environmental samples are delivered to a state-certified laboratory under chain-of-custody procedures, usually within 48 hs of sampling. Samples are maintained at approximately 4°C for shipping. Shipping containers are sealed with security tape to assure sample integrity during shipping. The chain-of-custody form should always accompany the samples delivered.

Soil Sampling Protocol

Soil samples should be collected in accordance with local, state, and national regulatory guidelines. Variations in local regulations, guidelines, and requirements do exist and can be quite large. Standard U.S. Environmental Protection Agency (EPA) methodologies for sampling and analysis are utilized routinely for environmental projects. When required, a work plan and permit application are submitted to and approved by the lead regulatory agency prior to beginning drilling or excavation activities. Soil cuttings and excess sampling materials should be properly stored and labeled on site in U.S. Department of Transportation (DOT) 17-H containers pending off-site disposal. Where excavated soil is left on site pending treatment or off-site disposal, it should be placed in a bermed area on high-density polyethylene (HDPE) liners, and covered with HDPE liners to prevent contaminated runoff or leakage.

Sampling Methods

Undisturbed samples are obtained using a slide hammer and core sampler with a single sampling cup at the end. The sampler typically contains one clean, 6- in.-long by 2- in.-diameter brass or stainless steel sample tube. The sample is obtained by hammering the cup and sampler into undisturbed soil. The sampler is retrieved and opened, and the sample tube containing the sample is extracted. Samples may be collected from tank pits and soil piles by driving a brass or stainless steel tube into the soil by hand. The top inch or two of soil at the sampling location is first removed to ensure a relatively fresh sample. Some analyses or guidelines allow for a disturbed sample to be dug using a trowel and then placed in a glass jar. Soil samples can also be obtained using handheld continuous-coring tools, typically 4 ft long and 1 in. in diameter. Made by a variety of manufacturers, these portable samplers are driven into the soil by hand using electric rotary or pneumatic hammers. After driving the sampler 3 to 4 ft deeper into the ground, the sampler is extracted and the inner sampling tube containing the sample is removed. The inner sample tubes are typically composed of polyethylene, brass, or stainless steel.

PreDrilling Precautions

The Underground Service Alert (USA) should be contacted between 2 days and 2 weeks prior to drilling. USA will contact local utility companies, which will identify the locations where buried utilities enter the property. Because utility companies do not identify buried utilities on private property, boring locations can be cleared using a magnetic line and cable locator. The exact location and number of borings at each site are usually marked in the field by the project scientist or engineer based on a prepared work plan.

Lithological Descriptions

Soils and unconsolidated deposits are commonly described according to ASTM Method D2488–84 and the U.S. Classification System (USCS) for physical description and identification of soils. Other soils identification systems, including the Burmister Soil Identification System for unconsolidated deposits, are commonly used with the USCS. The other soil description system is the Comprehensive Soil Classification System (CSCS) developed by the U.S. Department of Agriculture (USDA). The CSCS describes soils as to agricultural productivity potential and best agricultural land use.

The ASTM Soil Classification Flow Chart and the USCS are generally accepted soil description methods used in the engineering and environmental fields in the United States. Descriptions for moisture, density, strength, plasticity, and so on, are made using ASTM guidelines. Stratigraphic, genetic, and other data and interpretations are usually also recorded on the boring log. For consolidated deposits, including igneous, metamorphic, and sedimentary rocks, the USCS is combined with other geologic characteristics, such as weathering, sorting, sphericity, separation, and other features. The USCS soil classification system was originally developed by engineers and is in common use in the environmental field.

Other soil classification systems used primarily by soil scientists were developed by the Soil Survey Staff of the USDA in a handbook titled *Soil Taxonomy* (1975, revised in 1999). The World Reference Base (2000) developed a *Soil Resources Handbook* as well. The Australian soil classification was written by Isbell (1996, revised 2002).

Color is correctly described by comparing the soil sample with a Munsell Rock Color Chart (Munsell Color, 1988) and applying the correct designations and descriptions. If a Munsell chart is not available, colors should be described using only red, orange, yellow, green, blue, purple, brown, black, and white. Modifiers such as *light* or *dark* are acceptable. Dual color descriptions (e.g., yellow–brown) may also be used, but not descriptions such as *tan* or *buff*. The soil is described when moist or wet. Each stratum of soil is identified by the following items, in the order given: color, soil type, classification symbol, Munsell color designation (if any), consistency or relative density, moisture, structure (if any), and modifying information such as grain sizes, particle shape, cementation, plasticity, stratification, and so on. Soil classification varies based on the method. For example, the same acid sulfate soil might be described as follows:

- Hydraquentic Sulfaquept (U.S. Department of Agriculture, 1999)
- Orthithionic Fluvisol (World Reference Base, 2000)
- Sulfuric Redoxic Hydrosos by the Australian Soil Classification (Isbell, 1996, 2002)

Description of an acid sulfate soil using USCS categories:

- SP: 0 to 14 cm: very dark grayish brown, 95% fine grained, poorly sorted sand, with 5% silt, moist; yellow jarosite mottles in banded pattern, pH 2.7, gradational boundary to underlying unit; 100% recovery from core barrel.
- Description of an acid sulfate soil using *Soil Taxonomy* (1999) categories: Hydraquentic Sulfaquept, Bwj; 0 to 14 cm; very dark grayish brown (2.5Y 3/2) loamy fine sand; moderate coarse platy structure; friable; yellow jarosite mottles in a banded pattern, pH 2.7; gradational boundary to underlying unit; 100% recovery from core barrel.

Quality Control of Soil Samples: Duplicates

Small variations in soil lithology within several inches can lead to large differences in the results of the chemical analysis. Duplicate soil samples should be collected as close as possible to the actual soil sample, in the same lithologic zone. Duplicate soil samples, if required, are recommended to be collected at a minimum of 5% (1 in 20).

Monitoring Well Protocol

Wells are developed to remove residual drilling materials from the wellbore and to improve well performance by removing any fine material in the filter pack that can pass from the native soil into the well. Well development techniques include pumping, bailing, surging, jetting, and airlifting. In most cases, surging and pumping are satisfactory. A minimum of 12 h will lapse between placing the grout seal and well development. Development water is inspected for product sheen, odors, or sediments. Approximately 3 to 5 wetted casing volumes is removed during development. The well is considered fully developed when consistent pH, temperature, and conductivity readings (within 10%) indicate characteristic groundwater for the aquifer. A minimum of one wetted casing volume is removed between readings. Well casing volume is calculated in the following manner:

Diameter	Volume
(in.)	(gal/lin ft)
2	0.163
4	0.653

If the aquifer is slow to recharge, development will continue until the well is pumped dry. Development information is recorded on the water sampling data sheet. The data will include the following:

- Date of development
- Time of initial water-level readings
- Volume of water removed
- pH, temperature, conductivity, dissolved oxygen, and oxidation–reduction potential readings

Cross-contamination of wells from pumps is avoided by using dedicated equipment and proper decontamination procedures. All development water is stored in DOT-approved 55-gal drums, covered with lids, and labeled “Decontamination Water,” with the well number(s) and date of first accumulation. The development water is stored on site pending laboratory analysis, after which the water is disposed of properly.

Groundwater Data Collection

Monitoring of depth to water within wells at the site is conducted using a water-level meter. For consistency, all measurements are taken from the north side of the wellhead at the survey mark. To assess potential infiltration of fine-grained sediments. total well depth will also be measured. To reduce the potential for cross-contamination between wells, the monitoring is performed in order from least to most contaminated, if known. Wells containing free product are monitored last. The water-level measuring equipment is decontaminated between wells. Water-level data collected from the wells are used to develop a groundwater contour map for the project site. Groundwater flow is perpendicular to the equipotential lines drawn on the map.

Water Sampling from Monitoring Wells

For newly installed wells, a minimum of 24 to 72 h may be required to lapse between well development and sampling. If free product is detected, a product sample is sometimes collected for source identification. Where several chemical analyses are to be made for a given well, individual samples are collected in order of decreasing volatility. When the results from previous sampling events are known, it is recommended that the cleanest wells be sampled first, moving to the most contaminated wells later in the sampling event.

Cross-contamination between wells is avoided by careful decontamination procedures. Purging will proceed from the least to the most contaminated well, if known or indicated by field evidence. The well is purged until indicator parameters (pH, temperature, and conductivity) are stabilized (within 10%). A minimum of three wetted casing volumes is commonly removed by bailing or pumping. If the aquifer is slow to recharge, purging will continue until the well is pumped dry. Once the well is purged sufficiently, a sample may be collected after the water level has reached 80% of its initial volume. Where water-level recovery is slow, the sample may be collected after 2 h. Samples are collected using a disposable polyethylene bailer with a bottom siphon and nylon cord. If a Teflon or stainless steel bailer is used, it is decontaminated between wells. The groundwater in the bailer is inspected for free product. Samples are transferred to clean laboratory-supplied containers. Some regulators now allow micropurging, where minimal purging is carried out.

In Situ Remediation Systems

For remediation purposes, direct-push technology equipment, including both probe and CPT rigs, can provide a closely spaced liquid or grout delivery system for in situ remediation of soils and water affected by acid drainage. Monitoring wells, direct-push technology injection rods, and well points can be used for the delivery of in situ chemicals and grouts for treating acid drainage. These delivery ports can be used to inject:

1. Chemical reducing agents
2. Biocides to kill sulfide-oxidizing bacteria
3. Liquid or grout carbon substrates for creating fermentable anaerobic subsurface environments to lower dissolved oxygen content in groundwater and temporarily create reducing conditions
4. Liquid or grout neutralizing agents on close spacing

Even gas infusion using hollow-fiber membrane technologies can be used to change redox conditions or pH in 2-in.-diameter monitoring wells. Gas-phase reducing agents such as hydrogen (H_2), sulfur dioxide (SO_2), or hydrogen sulfide (H_2S), or neutralizing agents such as ammonia (NH_4), can be used with 2-in.-diameter monitoring wells. Gas solubility is increased when the gas infusion tool is covered by a larger water column in the well. Although gas, liquid, and grout injections are unlikely to fully treat the subsurface permanently, in situ applications may provide enough temporary treatment to prevent acid generation from beginning during a planned mine or development project. In situ treatment could be planned for implementation during field operations to maintain both anaerobic conditions within shallow aquifers and reducing conditions of potential acid sulfate soils. Once the mining or development project has been finished and site disturbance remediation has been completed, the use of alkaline or reducing treatment chemicals may be discontinued as the subsurface geochemistry reverts to neutral anaerobic conditions. In situ treatment requires detailed engineering design, bench testing, pilot testing, regulatory

approval, and a significant monitoring program.

References

American Society for Testing and Materials, 1984. Standard Practice for Description and Identification of Soils: Visual-Manual Procedure. Method D2488–84. ASTM International, West Conshohoken, PA.

California Department of Water Resources, 1981. California Well Standards. Bulletin 74–81, Sacramento, CA.

California Department of Water Resources, 1990. California Well Standards. Bulletin 74–90. DWR, Sacramento, CA.

California Regional Water Quality Control Board, 1989. Leaking Underground Fuel Tank (LUFT) Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. RWQCB, Sacramento, CA.

California Regional Water Quality Control Board, 2010. Leaking Underground Fuel Tank (LUFT) Field Manual: Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure. RWQCB, Sacramento, CA.

California Regional Water Quality Control Board, 1990. Tri-Regional Board Staff Recommendations for Preliminary Investigation and Evaluation of Underground Tank Sites. RWQCB, Sacramento, CA.

Driscoll, F.G., 1986. Groundwater and Wells, 2nd ed. Johnson Filtration Systems, St. Paul, MN, pp. 268–339.

Isbell, R.F., 1996. The Australian Soil Classification. CSIRO Publishing, Melbourne, Australia.

Isbell, R.F. 2002. The Australian Soil Classification, rev. ed. CSIRO Publishing, Melbourne, Australia

Jacobs, J.A., Kram, M., and Lieberman, S., 2000. #XII Direct push technology sampling methods. In: Standard Handbook of Environmental Science, Health and Technology, J. Lehr, ed. McGraw-Hill, New York, Chapter 11.

Kram, M., and Lieberman, S., 2000. #XI Cone penetrometer and direct push technology assessments, sampling and remediation. In: Standard Handbook of Environmental Science, Health and Technology. J. Lehr, ed. McGraw-Hill, New York, Chapter 11.

Munsell Color, 1988, Munsell Soil Color Charts. Munsell Color, Baltimore, MD.

Sisk, S.J., 1981. NEIC Manual for Groundwater/Subsurface Investigations at Hazardous Waste Sites. EPA-330/9-81-002. U.S. EPA, Denver, CO.

Testa, S.M., 1994. Geologic Aspects of Hazardous Waste Management. CRC Press, Boca Raton, FL, pp. 145–187.

U.S. Department of Agriculture, Soil Survey Staff, 1999. Soil Taxonomy, 2nd ed. Handbook 436. USDA, Washington, DC.

World Reference Base, 2000. WRB for soil resources. FAO. http://www.fao.org/ag/ag1/ag11/wrb/doc/wrb2006final.pdf.

APPENDIX F
CONVERSION FACTORS AND DATUMS

Multiply	By	To Obtain
	Length	
Inch (in.)	25,400	Micrometer (µm)
Inch (in.)	2.54	Centimeter (cm)
Inch (in.)	25.4	Millimeter (mm)
Foot (ft)	0.3048	Meter (m)
Mile (mi)	1.609	Kilometer (km)
	Area	
Acre	0.4047	Hectare (ha)
Acre	0.004047	Square kilometer (km^2)
Square mile (mi^2)	259.0	Hectare (ha)
Square mile (mi^2)	2.590	Square kilometer (km^2)
	Volume	
Gallon (gal)	3.785	Liter (L)
Cubic inch (in^3)	16.39	Cubic centimeter (cm^3)
Cubic inch (in^3)	0.01639	Liter (L)
Cubic mile (mi^3)	4.168	Cubic kilometer (km^3)
	Mass	
Ounce, avoirdupois (oz)	28,350	Milligram (mg)
Ounce, avoirdupois (oz)	28.35	Gram (g)
Pound, avoirdupois (lb)	0.4536	Kilogram (kg)
Ton, short (2000 lb)	0.9072	Metric ton (mt)
	Pressure	
Atmosphere, standard (atm)	0.1013	Megapascal (MPa)
Bar	0.100	Megapascal (MPa)
	Concentration	
Parts per billion, by weight (ppb)	0.001	Milligrams per kilogram (mg/kg)
Parts per million, by weight (ppm)	1	Milligrams per kilogram (mg/kg)
Per mil (‰)	1	Atoms per 1000 atoms
	Temperature	
Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows: °F = (1.8× °C)+32.		
Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: °C = (°F − 32)/32.		

References

Chisholm, L.J., 1967. Units of weight and measure - International (Metric) and U.S. Customary: U.S. National Bureau of Standards Miscellaneous Publication 286, 251 p.

U.S. Geological Survey, 1919. Hydraulic conversion tables and convenient equivalents (2d ed.): U.S. Geological Survey Water-Supply Paper 425-C, p. C71–C94.

U.S. Geological Survey, National Water Summary on Wetland Resources *United States Geological Survey Water Supply Paper 242, Feb.* http://water.usgs.gov/nwsum/WSP2425/conversion.html.

U.S. Geological Survey, 2013. Circular 1262, Conversion factors, water-quality units, and vertical datums; http://pubs.usgs.gov/circ/2003/circ1262/htdocs/conversions.html http://pubs.usgs.gov/circ/2003/circ1262/htdocs/conversions.html.

APPENDIX G
NOMENCLATURE AND PHYSICAL CHARACTERISTICS OF PYRITE

Nomenclature of Iron–Sulfur Compounds

Pyrite is naturally occurring FeS_2 and the compound has been called iron disulfide. It can also be referred to by its chemical name, iron(II) persulfide. It is believed that the iron and sulfur atoms in FeS_2 are arranged as Fe–S–S rather than S–Fe–S. S_2^{2-} is the persulfide and is the nomenclature analog of peroxide with oxygen (O_2^2). In FeS_2, iron is assigned an oxidation number of 2+, since persulfide has an oxidation number of 2−, where each sulfur atom is assigned an oxidation number of 1−. Although pyrite is the primary iron sulfide found on Earth, there are several other compounds containing iron and sulfur that could also be called iron sulfides.

Iron forms compounds primarily in the 2+ and 3+ oxidation states. Traditionally, iron(II) compounds are called ferrous iron (Fe^{2+}) and iron(III) compounds are called ferric iron (Fe^{3+}). Iron also occurs in higher oxidation states, an example being the purple K_2FeO_4, which is potassium ferrate, a purple compound that contains iron in its 6+ oxidation state. Iron(IV) is a common intermediate in many biochemical oxidation reactions (Nam, 2007). The oxidation states of sulfur in H_2S, S0 (elementary sulfur), SO_2, SO_3, and H_2SO_4 are, respectively; 2−, 0, 4+, 6+, and 6+.

Elements and Redox States

Iron: 2−, 0, 2+, 3+, and 6+ (as in FeO_4^{2-})

Sulfur: 2−, 0, 4+, 6+, and 6+ (as in H_2SO_4)

Iron Sulfides

FeS iron(II) sulfide

FeS_2 iron(II) persulfide (pyrite)

Fe_2S_3 iron(III) sulfide

Fe_3S_4 iron(II), (III) sulfide (spinel, greigite)

To balance the oxidation state of Fe_3S_4 requires a mixture of FeS and Fe_2S_3. For FeS, the iron is Fe(II), and for the Fe_2S_3, the iron is Fe(III). No iron has a 4+ oxidation state.

Physical Characteristics of Pyrite

Feature	Characteristics
Color	Pale brassy yellow.
Luster	Metallic.
Transparency	Crystals are opaque.
Crystal system	Isometric.
Crystal habits	Include the cube and frequently octahedron; crystal faces sometimes striated.
Cleavage	Very indistinct.
Fracture	Uneven and sometimes conchoidal.
Hardness	6.0 to 6.5.
Specific gravity	~ 4.95 to 5.10; sometimes 5.10+, which is heavier than average for metallic minerals.
Streak	Greenish black.
Solubility	Insoluble in water; however, catalyzed by iron- and sulfide-oxidizing bacteria in the presence of oxygen and water.
Other features	Brittle; striations on cubic faces caused by crossing of pyritohedron with cube (striations on cube faces also demonstrate pyrite's lower symmetry); pyrite (unlike gold) is not malleable.
Magnetism	Paramagnetic; paramagnetism is a weak form of magnetism in which the paramagnetic material is attracted only when in the presence of an externally applied magnetic field.
Associated minerals	Quartz, calcite, gold, arsenic, galena, fluorite, and others.
Best field indicators	Crystal habit, hardness, streak, luster, and brittleness.

Reference

Nam, W., 2007. High-valent iron(IV)–oxo complexes of heme and non-heme ligands in oxygenation reactions. Accounts of Chemical Research, vol. 40, no. 7, pp. 522–531.

APPENDIX H
SUMMARY OF U.S. EPA METHOD 1627 KINETIC TEST PROCEDURE FOR THE PREDICTION OF MINE DRAINAGE QUALITY

JAMES A. JACOBS

This appendix, based on U.S. Environmental Protection Agency (EPA) (2011), is provided to illustrate U.S. EPA Method 1627 for kinetic testing procedures. Acid–base accounting is widely used for hardrock and coal mine drainage prediction. Previous testing procedures may be limited to strata that have an appreciable net acid–base balance. In other words, if the pH contrast is great between that of the rock sample and a neutral pH of 7, kinetic testing can work for predicting mine drainage quality. However, mines with nearly equal amounts of acid and alkaline production potential have results that are ambiguous and difficult to interpret. Many mines fall into this category with less than clear results, making interpretation of the prediction of mine drainage quality difficult and imprecise at best.

The EPA developed Method 1627 to better predict mine drainage quality, and their document reflects case studies in coal mines, not in hardrock mines. Nonetheless, hardrock mine drainage quality is also difficult to predict. The work of Maest et al. (2005) and Kuipers et al. (2006) showed that predictions of water quality for hardrock mines in the western United States was completely inadequate based on current procedures and based on information contained in publically available environmental impact statements (EISs). The majority of the case study hardrock mines in the Maest and Kuipers work predicted a low potential for acid drainage in one or more EISs. Of the 25 case study mines, nine (36%) mines have developed acid drainage on site as of the date of the study. Of these nine mines, eight (89%) predicted low acid drainage potential initially or had no information on acid drainage potential. Nearly all the mines that developed acid drainage either underestimated or ignored the potential for acid drainage in their EISs. Clearly, improved prediction of future mine drainage quality is needed for both coal mine and hardrock mine settings.

In Method 1627, the EPA addresses the ambiguous results for mines with low amounts of sulfur and carbonates, where it is difficult to predict whether water quality will be alkaline or acidic over time. According to the EPA, Method 1627 is a standardized simulated weathering test that provides information that can be used to predict mine drainage quality that may occur from mining operations and weathering. Method 1627 is intended for use in determining probable hydrologic consequences and developing cumulative hydrological impact assessment data to support Surface Mining Control and Reclamation Act permit application requirements. The method can also be a tool with which to generate data used to design and implement best management practices and treatment processes needed by mining operations to meet EPA discharge compliance requirements at 40 CFR Part 434 (U.S. EPA, 2011).

The procedures in Method 1627 are directed toward the coal-mining industry and regulatory agencies; however, according to the EPA, Method 1627 may also be applicable to highway and other construction involving the cut and fill of potentially acid-producing rock, including that in hardrock mines. Method 1627 originated under the auspices of the Acid Drainage Technology Initiative (ADTI), a group of scientists from federal research and regulatory agencies, state regulatory agencies, the mining industry, environmental and mining consultants, and academia. The ADTI group members developed mine drainage

technology and procedures through consensus processes. Method 1627 has been referred to generically as the ADTI Weathering Procedure 2 (ADTI-WP2) in other publications. The method may be used in a fixed laboratory to predict water quality characteristics such as pH, acidity, and the solubility of metals of mine site discharges using observations from sample behavior under simulated and controlled weathering conditions. Method 1627 incorporates techniques similar to those already used into reproducible, documented, and validated procedures for widespread use. Method 1627 is based on procedures developed and evaluated in a series of single, multiple, and interlaboratory method validation studies using up to eight laboratories representing the mining industry, consultants and other support businesses, federal regulatory agencies, and universities.

Method 1627 is performance-based and the procedures can be modified to improve performance (e.g., to overcome interferences or improve the accuracy or precision of the results) provided that you meet all performance requirements in this method. The exception to the modifications are requirements indicated as “must” in the procedures. Requirements for establishing equivalency of a modification (see Table H.4) are based on method performance in an interlaboratory method validation study using data sets from seven laboratories, after outlier removal. For Clean Water Act uses, additional flexibility is described at 40 CFR Part 136.6. Modifications not in the scope of Part 136.6 or in this method may require prior review and approval.

Method Summary

The procedures described in this method include four main concepts:

1. The collection of representative samples
2. Preparation of samples
3. Controlled simulation of field weathering conditions
4. Leachate collection and analysis

Samples are crushed to pass through a $\frac{3}{8}$-in. wire mesh and characterized for neutralization potential (Sobek et al., 1978), total (percent) sulfur, and particle-size distribution. Samples are reconstructed from particle-size sieve separations to a specified particle-size distribution (by percent weight), exposed to simulated weathering conditions, and leached periodically over time (at least every three months) with CO_2-saturated, deionized reagent water. Throughout Method 1627 implementation, a CO_2–air mixture is added to the column and to the saturation water (leachate) to simulate field conditions. The leachate is collected and tested for pH, conductivity, net acidity, alkalinity, sulfate, dissolved metals, and other analytes as needed (U.S. EPA, 2011).

Limitations and Interferences

The purpose of Method 1627 is to characterize the water quality of mine site drainage. The method is limited primarily by the extent to which the rock, sediment, or soil sample and simulated weathering conditions approximate actual site conditions. This scaling factors from obtaining chemical data from reactions in a 1-L bottle are a limitation that also affects many laboratory bench testing studies. The reproducibility of the testing and whether the samples are clearly representative of site conditions is the reason that significant effort should be taken to plan out the field sampling plan prior to going into the field to collect samples of various media.

The degree of representation is highly dependent on sample collection, storage, and preparation. Preparation variations include the level of crushing, mixing, and particle-size distribution, and simulated weathering conditions can vary with the procedures for water handling, gas mixing, and saturation and drying cycles. Method 1627 includes procedures needed to produce reliable prediction results under standardized conditions: evaluation of the quality and consistency of the sample collection and storage procedures, changes made to the sample between collection and preparation, such as sample crushing and reconstruction, and the similarity of the simulated weathering to actual site conditions such as percent humidity, partial pressures of gases, and saturation/drying cycles. It is not possible to collect a rock, sediment, or soil sample from the field for evaluation in the laboratory without disrupting the in situ particle-size distribution through collection mechanisms and crushing. Method 1627 contains requirements to ensure that results represent standardized sample structure and weathering conditions.

Surface Area/Volume Ratio

The ratio of the total surface area of the sample to the volume of water that is added and collected during each saturation cycle can determine the extent to which water comes into contact with the sample location in the field. A site conceptual model reflecting an understanding of groundwater fluctuations and surface water movements is necessary to obtain the most representative media samples from the best sample locations. In general, the laboratory sample test column diameter should be a minimum of four times the diameter of the largest particle as determined by Potter (1981) and Cathles and Breen (1983). This ratio is recommended for samples with grain sizes exceeding 0.5 cm (0.2 in.). For smaller particles, a factor greater than 4 should be used. Scaling factors that consider the ratio of column dimensions and particle size are presented by Murr et al. (1977). This method specifies a maximum sample particle size of $\frac{3}{8}$ in. (see Table H.2) and uses 2-in.-diameter columns. Method 1627 contains a requirement and procedures for reconstructing samples from sieved sample portions using a specific particle-size distribution (by weight percent) in the reconstructed samples. Reconstructed sample particle-size distribution is provided in Table H.2.

Surface Area

Although particle-size distribution can be used to calculate the surface area of a given sample, it often fails to indicate the total surface area that is, or can be, contacted by water in the column (i.e., soil particle surfaces can contain pores and other surface characteristics that are not recognized by sieve measurements). If equipment is available, the analyst should consider performing an assessment of particle surface area such as the Brunauer, Emmett, and Teller (BET) gas sorption analysis described by Brunauer et al. (1938). This assessment provides information for determining rates in terms of milligrams per surface area per day.

Sample Characterization and Leachate Analysis

Given adequate carbonate minerals in the sample and sufficient contact time, the water in the columns may reach saturation with respect to calcite at conditions appropriate for 10% CO_2. When the leachate is being drained, it will evolve toward equilibrium with the air outside the column. This results in a degassing of CO_2 from the leachate and an increase in pH. If the water was at or near calcite saturation while in the column, degassing of CO_2 during collection of the leachate may result in the supersaturation of calcite in the leachate. This process is explained in Hornberger et al. (2003). This method describes procedures for collection of leachate to minimize CO_2 degassing. Additional potential interferences that may be encountered during leachate analyses are specific to the analytical methods used to characterize

the leachate. These interferences and procedures for overcoming the interferences are discussed in the individual analytical methods listed in Tables H.1 and H.3.

Safety

Method 1627 does not address all safety issues associated with the use of the procedure. Each laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration regulations for the safe handling of chemicals, including reagents, hazardous sample media, and other chemicals specified in this method or in the methods used to characterize samples (see Table H.1) or analyze leachate (see Table H.3). A reference file of material safety data sheets (MSDSs) should be made available to all personnel involved in the chemical analysis. Extreme caution should be taken when handling pressurized gas cylinders and the gas introduction procedures described in this method. Columns should be assembled and maintained in a hood or otherwise well-vented area to control continuous venting of column offgases.

Table H.1 Sample Characterization and Appropriate Methods for Use with Method 1627

Characteristic	Method
Neutralization	Sobek et al. (1978) (EPA-600/2-78-054);
potential	Skousen et al. (1997)
Total sulfur	ASTM D3177, ASTM D4239, ASTM D2492

Source: U.S. EPA (2011).

Apparatus and Materials

Columns consist of vertical tubes or cylinders that are constructed to contain a sample of $\frac{3}{8}$-in. maximum particle size and to allow for transport and/or holding of gases and water (Figure H.1). Water and/or gases are introduced into and drained from the bottom of the column to eliminate air entrapment, simulate various groundwater conditions, and maximize contact with particle surface area (Figure H.2).

Figure H.1 Laboratory column setup for kinetic testing according to Method 1627. (From U.S. EPA, 2011.)

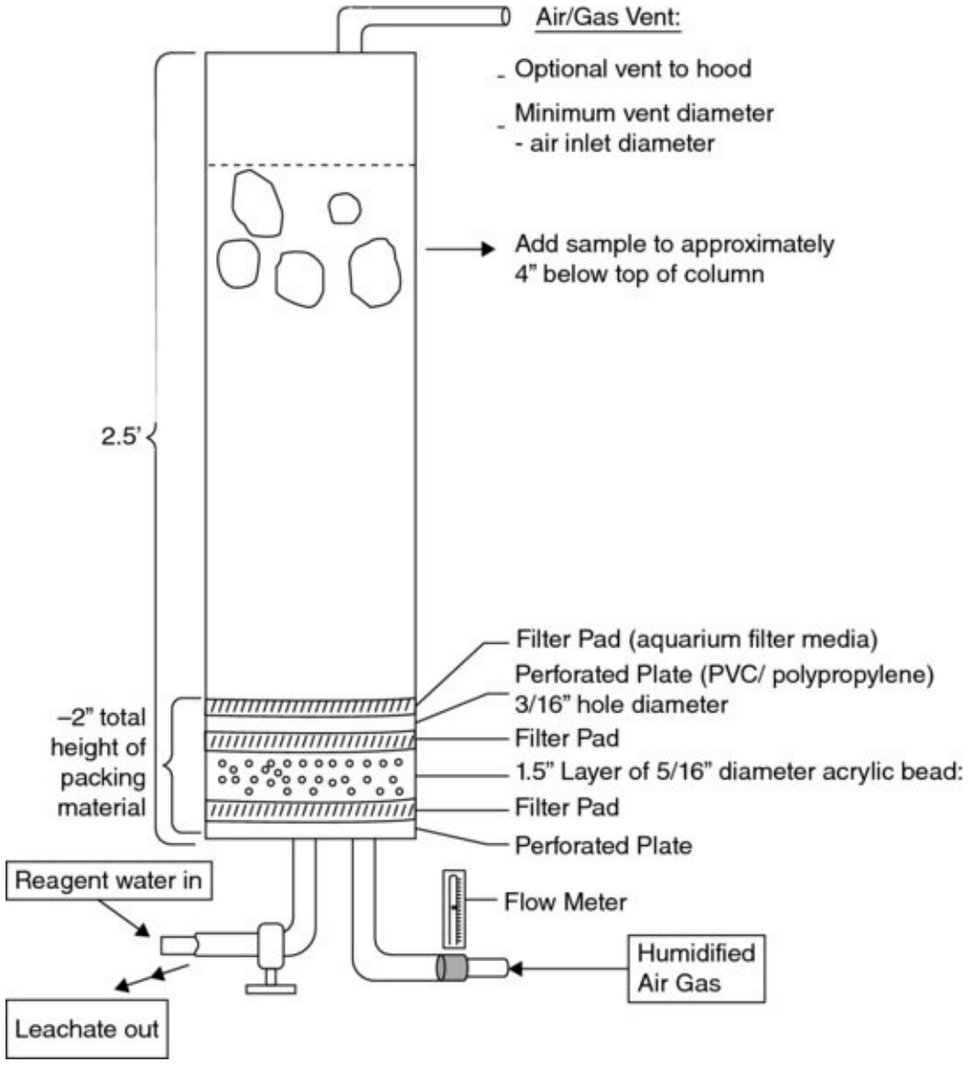


Figure H.2 Laboratory leaching column for kinetic testing according to Method 1627. (From U.S. EPA, 2011.)

Column Apparatus

The column is constructed of a transparent polycarbonate or polystyrene cylinder with an inner diameter of 2 in. Use of polycarbonate, polystyrene, or a similar transparent material is recommended by Method 1627 so that sample conditions can be observed during addition of the sample to the column and throughout the weathering and leaching procedures. A detailed list of other products to construct the column for Method 1627 follows.

Column. 2-in. clear rigid schedule 40 PVC pipe; U.S. Plastic Part 34107 or equivalent.

Column seals. Columns are sealed at the bottom and include a removable cap that contains a port for measuring and venting gases. 2-in. clear rigid schedule 40 PVC fittings, cap slip, U.S. Plastic Part 34296 or equivalent. Used to seal the top and bottom of the column.

Column Ports. Ports are inserted into the top and bottom of the column to allow introduction of mixed gases and water, leachate collection, and gas venting.

Air/gas introduction and venting ports. Threaded/barbed elbows, nylon, thread ¼-in. NPT, tube ID ¼ in. (U.S. Plastic Part 64301 or equivalent) or polypropylene, thread ¼-in. NPT, tube ID ¼ in. (U.S. Plastic Part 64482 or equivalent).

Leachate drainage port. Nylon, threaded ¼-in. NPT, tube ID ⅜ in. (U.S. Plastic Part 64794 or equivalent).

Column tubing and clamps. Column ports are connected to tubing that is oriented to allow gravity flow of water into the column, drainage of water from the column, and introduction and venting of gases (see Figure H.2). Clean flexible tubing should be used to provide greater control of water and gas flow. Recommended tubing sizes are 0.25 in. (gas mixture) and 0.5 in. (reagent water). Tubing should be tied to the column port using a hose clamp or equivalent.

Vinyl tubing. Used for tubing that will not require clamping (e.g., manifold, gas lines, tubing from gas source to humidified gas reservoir). ¼-in. ID and $\frac{3}{8}$-in. OD, $\frac{1}{16}$-in. wall thickness (Fisher Scientific Part 141697C or equivalent).

Rubber tubing. Used for tubing that will require clamping (e.g., water introduction and drainage tubing, tubing from humidified gas reservoir to column). Thick wall, rubber latex tubing. ¼-in. ID, $\frac{7}{16}$-in. OD, $\frac{3}{32}$-in. wall thickness (Fisher Scientific Part 14-178-5D or equivalent).

Plastic tubing clamps. Used on latex tubing for quick, total shutoff of gases or fluids. Fits ⅛- to ½-in. tubing. (Fisher Scientific Part 5869 or equivalent) *or* Thermo pinch-tight tube clamps (McMaster–Carr Part 5031K13 or equivalent).

Fixed-jaw clamps. Used on latex tubing to adjust gas flow (Fisher Scientific Part 05870A or equivalent).

Nylon tees. Used to connect tubing. Tube ID ½- and ¼-in. (U.S. Plastic Parts 64349 and 64346 or equivalent).

Couplers. Used to connect tubing. Tube ID ¼-in. nylon or PVDF (U.S. Plastic Parts 64322 and 64437 or equivalents). Tube ID ½-in. nylon (U.S. Plastic Part 64325 or equivalent).

Column lining. To allow uniform introduction of water and gases into the column, the bottom (up to approximately 5% of the total column height) contains several layers of filter and support materials (refer to Figure H.2). Reagent water and gas mixtures are introduced through the plates, beads, and filter material and into the sample via ports in the bottom of the column. These layers consist of two PVC or polypropylene perforated plates, three layers of filter material (aquarium filter media, and a 1½-in. layer of $\frac{5}{16}$-in.-diameter acrylic or glass beads. The layers should be added as presented in Figure H.2 and are intended to trap the smallest sample particle size but not result in clogging. Glass wool has been shown to neutralize acid and elevate pH in experimental work at both the Minnesota Department of Natural Resources and the U.S. Bureau of Mines. It should not be used for Method 1627 in this type of testing unless it is tested and shown to be nonreactive with the samples, reagents, and other products.

Perforated sheets. Polypropylene, natural, $\frac{3}{16}$-in. thickness, $\frac{3}{16}$-in. hole diameter, staggered rows (U.S. Plastic Part 42562 or equivalent) *or* PVC perforated sheets of the same thickness and diameter in staggered rows (U.S. Plastic Part 42562 or equivalent).

Plastic beads. Polypropylene, ½-in. diameter (U.S. Plastic Part 91539 or equivalent) *or* HDPE $\frac{5}{16}$-in. diameter (U.S. Plastic Part 91547 or equivalent).

Filter pads. Marineland bonded filter pads, 312 in^2, cut into circles to provide three filter pads to a line column (Petco Part SKU:237531 or equivalent).

Gas Mixture

Gases are mixed to a ratio of 90% air to 10% CO_2 using either a certified gas mixture, two-stage gas

cylinder regulators, flowmeters, mixing valves (gas proportioners), or flow valves.

Gas introduction. Once mixed, gases are introduced into the reagent water in the reagent water reservoir through a bubbler or porous stone below the water surface. The humidified gas mixture is maintained at the same temperature as the column (i.e., 20 to 25°C ± 3°C) and is introduced continuously through the column at a ratio of 9 : 1 air/CO_2 (Figure H.3).

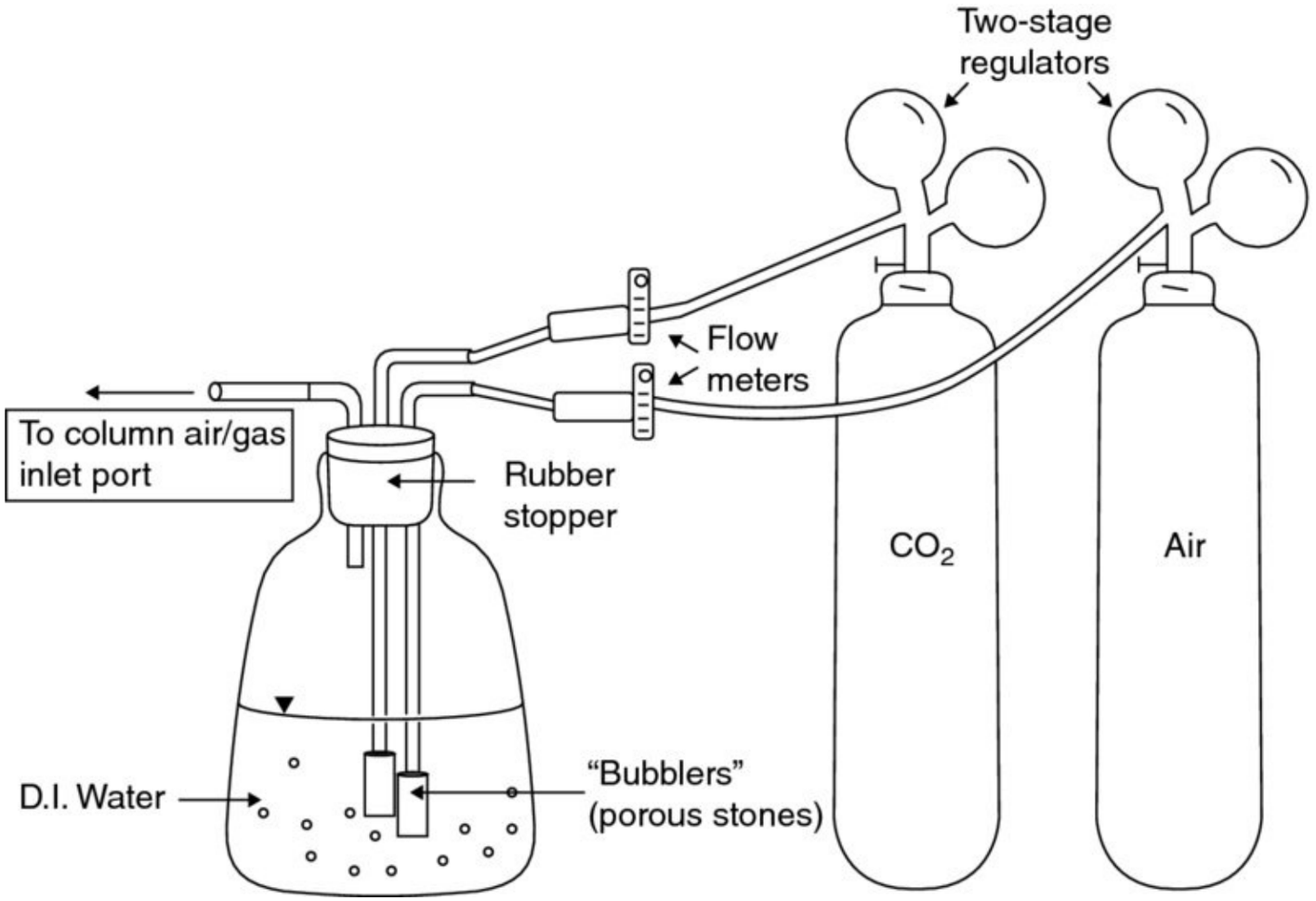


Figure H.3 Humidified air/gas apparatus according to Method 1627. (From U.S. EPA, 2011.)

Gas monitoring. Gas flow must be introduced continuously to maintain constant positive pressure and must be monitored daily using flowmeters, gas meters, or tube indicators (e.g., Draeger tubes) to ensure positive flow and to ensure that the concentration of CO_2 in the outflow gas is at least 10% (Bacharach Model 10-5000, with a tolerance of ±0.5%, or equivalent).

Tubing clamps. Fisher 05–871A (swivel jaw) or 05-870A (fixed jaw), or equivalent, is used to control gas flow through the tubing into the columns. Use of a flow regulator and meter is recommended to maintain a flow rate of approximately 1 L/min of the mixed humidified gas into the column (Omega Model FL3817-V rotameter or equivalent).

Rotameters. Capable of controlling the flow at approximately 1 L/min. Rotameters should be used between the gas source and the reagent water reservoir, and between the reagent water reservoir and each column (TC-Omega Part FL-817-V or FL-815-V or equivalent).

Tubing connectors. Threaded, barbed elbows, 0.12 × 0.25 in., used to connect rotameters to inlet and outlet tubing (U.S. Plastic Part 64758 or equivalent).

Reagent water reservoir. A water bottle or carboy is half-filled with reagent. The bottle is sealed with a rubber stopper containing inlet and outlet ports for the introduction and release of the mixed gases (see Figure H.3).

Carboy. 2.5-gal carboy. Carboys with handles provide support for bungee cords needed to hold the stopper in place (U.S. Plastic Part 75029 or equivalent).

Rubber stopper. Two-hole, with a third hole drilled into the stopper at a distance sufficient to allow a bungee cord to secure the stopper in place once tubing is inserted (Thomas Scientific Part 8742S20 or equivalent).

Ridged tubing. $\frac{5}{16}$-in.-ID extruded ridged tubing, inserted into holes in the stopper to provide support for flexible tubing; inlet and outlet tubing is attached to ridged tubing (U.S. Plastic Part 44018 or equivalent).

Gas outlet port. Tubing is fitted through and just below the rubber stopper into the headspace remaining in the reservoir.

Reagents

Gas Mixture

A mixture of humidified air and CO_2 at a ratio of 9 : 1. This mixture is introduced continuously into the column.

Carbon dioxide (CO_2). Industrial grade; gas cylinders or liquid CO_2 (i.e., Dewars) may be used.

Air. Industrial-grade compressed air at approximately 21% O_2, 78% N_2; alternatively, house air may be used. An industrial-grade premixed compressed gas cylinder containing $O_2/CO_2/N_2$ at a ratio of 1 : 1 : 8 may be used as an alternative to combining the gases. Caution: The introduction of oil contaminants into weathering columns can significantly affect the results of this method. If house air is used, it must be run through an in-line filter to ensure that all oil is removed.

Reagent Water

Reagent water is prepared by distillation, deionization, reverse osmosis, or other technique that removes potential interferences (e.g., metals and organics).

Reagents for Sample Characterization and Leachate Analysis

Reagents required for sample characterization and leachate analyses are specific to the analytical methods used and are provided in the individual analytical methods listed in Tables H.1 and H.3.

Sample Collection, Preservation, and Handling

Sample Collection

Collect representative bulk samples using air-rotary drilling, core drilling, or extraction from highwall, roadcut, or outcrop exposures. Collect samples using standard procedures described by Sobek et al. (1978), Block et al. (2000), Griffiths (1967), and Tarantino and Shaffer (1998). Approximately 2000 g of sample is needed to fill a single column as described in this method.

Documentation

Record the location, date, time, and amount of sample collected.

Sample Crushing and Splitting

Prior to method implementation, bulk samples must be crushed to a maximum particle size of ⅜ in. To demonstrate the accuracy of results, it is recommended that at least two identical homogeneous sample aliquots be prepared from each bulk sample. Crush bulk samples into $\frac{3}{8}$-in. fractions using a jaw crusher. The first portion of sample that is crushed should be run through a screen or sieve to ensure that the crusher is set to the appropriate size. After the entire sample is crushed, it is riffled through a bulk splitter with openings set to approximately 1.5 in., and split using a riffle splitter or similar piece of equipment to get identical representative splits of the total sample volume. These procedures are described in ASTM C702-98 and by Noll et al., 1988.

Sample Shipment, Storage, and Preservation

From the time of sample collection until method implementation, some oxidation of pyrite can occur, resulting in soluble acid-sulfate salts. Prior to method implementation, samples should be stored in sealed HDPE containers, or some other airtight container, under dark, dry, and cool conditions. For small sample sizes, opaque Nalgene bottles may be used. Crushed samples should not be stored for longer than 6 weeks. Sample shipment, storage, and preservation procedures are described in ASTM D5079.

Procedure

Sample Preparation

Sample sizing. Pass the sample through a ⅜-in. mesh to ensure that no particle sizes greater than ⅜ in. are added to the column. Following this sizing, determine the particle size distribution of the sample using at least five dry sieves (i.e., sieves No. 4, 10, 16, 35, 60). For analysis of particle-size distribution, use U.S. sieves or sieves of equivalent mesh size (e.g., U.S. No. 16 = Tyler No. 14). Approximately 2 kg is needed for each column. If additional information is needed to determine the surface area or if method results will be used to determine reaction rates in milligrams per surface area per day, the analyst may want to consider using additional sieves, the Malvern system of laser diffraction, or assessment of particle surface area (e.g., BET gas sorption analysis).

Sample characterization. Prior to method implementation, samples should be analyzed for neutralization potential (NP) and percent total sulfur. Methods for analysis of these parameters are included in Table H.1. If the overall change in particle size, NP, percent sulfur, or other parameters will be determined, these analyses may also be performed on the sample after the last leachate sample has been collected and the sample is removed from the column. Additional parameters may be measured if required or requested by the data user. Any approved ASTM, U.S. Geological Survey (USGS), EPA, Association of Official Analytical Chemists (AOAC), or Standard Methods analytical method may be used for sample characterization, according to the U.S. EPA (2011).

Sample reconstruction. Once samples have been collected and crushed, sample particle-size distribution that occurred in the field is lost. The size distribution provided in Table H.2 is intended to provide standardized conditions and to facilitate uniform exposure of samples to weathering conditions and collection of leachate. Using the sieved sample portions, reconstruct samples into particle-size

distribution portions according to the weight percentages specified in Table H.2.

Table H.2 Particle-Size Distribution of Reconstructed Samples for Use with Method 1627

U.S. Sieve No. (or Equivalent Mesh Size)	Percent of Sample (by Weight)
3/8 in. to 4	40
4–10	25
10–16	15
16–35	10
35–60	5
Less than 60	5
Total	100

Source: U.S. EPA (2011).

Column Preparation

Filling the column. Uniform exposure of the sample to weathering conditions is critical to method performance. Using a standardized rock density table such as the Blaster's Guide, determine the approximate total weight of sample needed to fill the column to 4 in. below the top. Approximately 1800 to 2000 g should be sufficient to fill a column 2.5 ft in height and 2-in. in diameter. Using a wide-bore or powder funnel, add approximately 2000 g of the reconstructed sample to the column, being careful to ensure uniform distribution with little to no packing. The top of the sample should be at least 4 in. below the top of the column to prevent loss of sample or leachate water during test implementation. Weigh the sample before adding it to the column. The total weight of the sample added to the column must be recorded to the nearest 1.0 g for use in result calculations.

Column maintenance. Maintain the column at a temperature between 20 and 25°C ± 3°C. Check the column daily to ensure that temperature and gas flow are maintained. The temperature must be recorded at least daily and remain constant. If data will be used for assessment of reaction kinetics or gas mixture partial pressure assessments, the data should be adjusted for temperatures outside the range 20 to 25°C. Using a portable CO_2 meter capable of measuring CO_2 to 10% (within 0.5%); take daily readings of the CO_2 released from the column exhaust.

Simulated Weathering Procedure

The simulated weathering procedures described here consist of alternating cycles of saturation and humidified gas mixture. These procedures are recommended for evaluation of overburden in nonarid regions or areas where there may be variably saturated conditions. Alternative procedures may be used provided that they are designed to assess site conditions and meet the reproducibility performance standards of Method 1627.

Initial column flush. Once the column has been filled with sample, reagent water is introduced through the water inlet port (refer to Figure H.2) until the column is full and all visible pore spaces are saturated. Gently tap the column to fill any visible air pockets with water. Alternatively, a thin wire may be inserted into the column to adjust the sample and ensure saturation. Allow the reagent water to sit in the column for approximately 1 h prior to collecting and analyzing the initial flush water for conductivity. Continue to

add, drain, and analyze reagent water in this manner until the conductivity of the water stabilizes (relative standard deviation between conductivity measurements 20% or less). Composite the flush water collected into a single composite water sample, and analyze using the same procedures as those used to analyze the water samples collected following each 24-h saturation period. The volume of water added to and collected from the column should be recorded with each flush. These volumes should also be recorded during each weekly saturation period.

Humidified air cycles. Once the column has been drained of the final initial flush sample, the humidified gas mixture is introduced continuously through the gas inlet port at the bottom of the column (see Figures H.1 and H.2). The column is allowed to sit for a period of 6 days during the humidified air cycle. This cycle is repeated after each saturation cycle.

Saturation cycles. Following each humidified air cycle, reagent water is introduced through the water inlet port to just above the sample surface. If necessary, gently tap the column to fill any visible air pockets with water. The volume of water added must be recorded. If the introduction of water into the column through the bottom port is difficult or slow, a pipette bulb can be used to create a vacuum to pull water up and into the column. Once water has been added, clamp the water inlet tube shut, as close as possible to the column, to ensure that the water collected at the end of the saturation period has been in sufficient contact with the sample. Record the volume of water added to the column.

Gas introduction. Once the column has been saturated according to procedures, introduce the gas mixture into the sample through the gas inlet port at the bottom of the column until a slight positive pressure is reached, such as a small outflow produced through the air vent in the top of the column. Gas flow can be controlled and maintained at approximately 1.0 L/min using a combined flow regulator and meter (e.g., Omega FL-3817-V series rotameter or equivalent). Care should be taken to avoid displacing the water during gas introduction. Gas should be introduced slowly until a slight positive pressure is reached.

Leaching. Allow the column to sit for a period of 24 h in this saturated condition. Following this 24-h period, drain the column and collect the leachate, then repeat the humidified air cycle. The saturation cycle is repeated every week until method implementation is complete (for up to a minimum of three months).

Leachate Collection and Analysis

Leachate collection. Following each 24-h saturation cycle, the water or leachate is drained from the column and collected for analysis. Leachate is drained from the column through the water inlet tubing by disconnecting the tubing from the water source. The procedure used to collect leachate must minimize carbon dioxide degassing by inserting the drainage tube into the bottom of the sample collection container throughout collection; seal the container immediately following sample collection; refrigerate the sample if analysis is not performed immediately; keep the sample container submerged in ice if collection drainage is slow). The total volume added to and collected from each column must be measured and recorded prior to water analysis. Analyze the leachate immediately for determination of pH and conductivity, and prepare additional aliquots for further analysis. If the leachate will be analyzed for dissolved parameters (SO_4^{2-}, metals), the leachate must be filtered through a 0.45-µm filter prior to analysis.

Leachate analysis. The leachate is analyzed for target parameters using approved methods. Recommended analytical methods are listed in Table H.3. Specific conductance (conductivity), alkalinity, and pH are analyzed as soon as possible after collection. Leachate that will not be analyzed immediately for measurement of other parameters (e.g., metals, sulfate) must be preserved and stored according to the

requirements specified in the analytical method(s) to be used.

Table H.3 Analytes and Appropriate Methods for Use with Method 1627[a]

Analyte	Method
pH	EPA 150.1; Std. Methods 4500-H; ASTM D1293; USGS I-1586
Dissolved metals[b] (e.g., Fe, Mn, AI, Mg, Ca, Se)	EPA 200.7, 236.1, 236.2; Std. Methods 3111, 3113, 3120; ASTM D1068; USGS I-3381
Sulfate	EPA 375.1, 375.2, 375.4; Std. Methods 4500
Alkalinity (to pH 4.5)	EPA 310.1, 310.2; Std. Methods 2320B; ASTM D1067; USGS I-1030, I-2030
Acidity/net acidity (to pH 8.2)	EPA 305.1; Std. Methods 2310; ASTM D1067
Specific conductance	EPA 120.1; Std. Methods 2510B; ASTM D1125; USGS I-1780

Source: U.S. EPA (2011).

[a]Any approved ASTM, USGS, EPA, AOAC, or Standard Methods analytical method may be used for leachate analysis.

[b]The analytes measured will depend on specific permit needs or other intended uses of the data.

Quality Control

All quality control measures described in the analytical methods for leachate analysis (Table H.3) and sample characterization (Table H.1) should be used for Method 1627.

Blanks

Inert material is to be used such, as clean, well-characterized quartz chips or sand of requisite particle size is run along with samples to check for unexpected contributions from the test apparatus and reagents.

Duplicate Samples

Duplicate samples are prepared according to Method 1627 procedures. Identical sample masses and leaching volumes are used, and samples are exposed to identical simulated weathering conditions. At a minimum, at least one sample from each mine site must be run in duplicate. If there are more than 10 samples per site, 10% of the total number of samples must be run in duplicate. If necessary, the leachate from duplicate samples can be analyzed using a staggered approach. In this case, pH and conductivity are measured weekly from both the primary and duplicate columns. Analytes not requiring immediate measurement, such as metals, are measured weekly in leachate from the primary column but every other week in leachate from the duplicate column. Analysis of these samples gives a measure of the precision described as relative percent difference (RPD) associated with sample preparation and with laboratory procedures. RPDs between results of duplicate samples are calculated for each analyte [using equation (H.1)] and should not exceed the RPDs listed in Table H.4.

$$\mathrm{RPD} = \frac{|C1 - C2|}{(C1 = C2)/2} \times 100\% \qquad \text{(H.1)}$$

where C1 is the concentration in the primary sample and C2 is the concentration in the duplicate sample.

Table H.4 Analytes and Appropriate Methods for Use with Method 1627

Analyte	14-week RPD	Initial Flush RPD	Weathering Test RPD (Difference Between 14-Week and Initial Flush RPD)
Fe	90.4	50.9	39.5
Mn	52.5	44.1	8.4
AI	72.5	38.6	33.9
Ca	21.9	38.8	(16.9)[a]
Mg	21.4	16.4	5.0
Se	42.9	26.2	16.7
Zn	60.2	52.0	8.2
Na	25.1	21.1	4.0
K	23.7	21.5	2.2
SO_4	27.5	20.4	7.1
Alkalinity	28.7	35.2	(6.5)[a]
Acidity	99.9	27.0	72.0
Conductivity	13.2	11.1	2.1
	Mean absolute difference:		
pH	0.2	0.2	0

Source: U.S. EPA (2011).

[a]Relative percent difference between analyses were greater between samples collected during initial flush than between weekly samples.

Calculations and Results

Analytical data should be reported initially in units of mg/L for aqueous (leachate) samples and mg/kg or percent for solid (overburden characterization) samples. Results may also be reported in parts per thousand (ppt). Report total sample weight and leachate volume. The mass of each analyte weathered from the sample each week can be calculated using the equation.

$$\text{analyte (mg)} = (\text{mg/L}) \times \text{leachate volume out (L)} \quad \text{(H.2)}$$

Acid production or metals release per weight of sample can also be determined by dividing the result in equation (H.2) by the weight of the sample exposed to weathering conditions.

Evaluation of the weathering data can be performed to support permitting decisions and developing special handling plans for selected overburden strata. These data can be used alone or in combination with data resulting from other mine drainage prediction tools (e.g., acid–base accounting, x-ray diffraction). Typically, in acid–base accounting (ABA) the total sulfur and neutralization potential would be determined for all overburden samples, and the weathering test described in this method would be performed on selected samples where the ABA was inconclusive.

For permitting decisions the method can be used to determine whether inconclusive samples have alkalinity exceeding acidity. This is the most fundamental question in evaluating overburden analysis data.

Using ABA, a rock sample with a total sulfur content of 1% would have a maximum potential acidity of 31.25; if the rock sample had an NP of 31.25, it would be interpreted that the acidity and alkalinity would be equal, or zero. The total sulfur content is a surrogate measurement of the potential acidity, and the NP is a surrogate of actual alkalinity. The kinetic test method produces a leachate that can be analyzed for the actual acidity and alkalinity produced by the sample.

Using ABA, it is not possible to obtain any measurement or accurate estimate of the potential for production of iron, manganese, aluminum, or other metal of concern. The kinetic test method produces a leachate that can be analyzed for any metal concentration. However, the user of the method should consider the iron concentration, for example, to be an accurate and precise measurement of the iron in the leachate and not necessarily an accurate measurement of the effluent from a mine site. In this respect, the iron concentration can be used to indicate which rock samples may cause an iron problem at the mine site, not a number that should be compared to the effluent limitations for compliance purposes.

Since the weathering test is conducted for at least three months, longer if appropriate, a simple time plot should be constructed to determine if there are any trends in the data. For example, plots of acidity and sulfate should be made to determine if there is an increase through time that would indicate that acid mine drainage is likely to be produced from that lithologic unit. In addition, time plots of alkalinity and calcium should be constructed to determine if there are trends in the alkalinity or calcium data that would indicate that alkalinity production or calcite dissolution is occurring from selected rock samples. Understanding the reaction kinetics of the rock samples weathering within the leaching columns (and in the mine environment) is the ultimate goal of this method.

Questions

1. If a rock sample is a shale from a marine paleoenvironment with a pyritic sulfur content of 0.8% and an NP of 80 tons per 1000 tons of calcium carbonate equivalents, does the weathering pattern have

   the characteristic shape of a diffusion-controlled process? (The characteristic shape of a diffusion-controlled process would plot as the square root of time.)

2. Can we predict that the rate of pyrite oxidation will be offset by the rate of calcite dissolution, and will the pyrite be depleted before the calcite? Refer to Brady et al. (2004), Langmuir (1997), Lasaga (1998), and White (1986).

Method Performance

The RPD results listed in Table H.4 reflect the pooled results of the interlaboratory study, using data sets from seven laboratories evaluating the effects of weathering on samples of Brush Creek shale, Kanawha Black Flint shale, Lower Kittanning shale, Houchin Creek shale, and Middle Kittanning sandstone. Method precision was assessed using results of duplicate samples exposed to identical weathering procedures. RPDs were pooled for leachate samples collected over a 14-week period.

Record Keeping

Proper daily and weekly documentation is necessary with Method 1627. An example daily reporting sheet is shown as Figure H.4 and a weekly reporting form is shown as Figure H.5.

Sample ID:						
		Column 1		Column 2		
Date / Time	Temp. °C	Flow (Lpm)	% CO_2 (in exhaust)	Flow (Lpm)	% CO_2 (in exhaust)	Notes

Figure H.4 Daily monitoring reporting form for use with Method 1627. (From U.S. EPA, 2011.)

Sample ID:							
Date / Time	Week #	Water In (mLs)	Water Out (mLs)	pH	Conductivity (µmhos/cm)	Alkalinity (to pH 4.5) mg/L as CaCO3	Acidity (to pH 8.2) mg/L as CaCO3
	Initial Flush						
	Week-1						
	Week-1						
	Week-2						
	Week-2						
	Week-3						
	Week-3						
	Week-4						
	Week-4						
	Week-5						
	Week-5						
	Week-6						
	Week-6						
	Week-7						
	Week-7						
	Week-8						
	Week-8						
	Week-9						
	Week-9						
	Week-10						
	Week-10						

Figure H.5 Weekly monitoring reporting form for use with Method 1627. (From U.S. EPA, 2011.)

References and Suggested Reading

American Society for Testing and Materials, 2000. Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell. D5744-96. Annual Book of ASTM Standards, 11.04. ASTM International, West Conshohocken, PA, pp. 257–269.

Appelo, C.A.J., and Postma, D., 2005. Geochemistry, Groundwater and Pollution, 2nd ed. A.A. Balkema, Leiden, The Netherlands, 649 pp.

Block, F., Tarantino, J., Hornberger, R.J., Brady, K.B.C., Donovan, J., Sames, G., and Chisholm, W., 2000. Overburden sampling considerations. In: Prediction of Water Quality at Surface Coal Mines. Acid Drainage Technology Initiative, Colorado School of Mines, Dolden, CO.

Brady, K.B.C., and Smith, M.W., 1990. Pyritic sulfur analyses for coal overburden: differences between laboratories. In: 1990 National Symposium on Mining, University of Kentucky, Lexington, KY, pp. 53–58.

Brady, K.B.C., Hornberger, R.J., Scheetz, B.E., and Loop, C.M., 2004. Refinement of ADTI-WP2 standard weathering procedures, and evaluation of particle size and surface area effects upon leaching rates, Part 2; Practical and theoretical aspects of leaching kinetics. In: Proceedings of the 21st National Conference, ASMR, and 25th West Virginia Surface Mine Drainage Task Force Symposium. American Society for Mining and Reclamation, Lexington, KY, pp. 174–200.

Brunauer, S., Emmett, P.H., and Teller, E., 1938. Journal of the American Chemical Society, vol. 60, p. 309.

Cathles, L.M., and Breen, K.J., 1983. Removal of Pyrite from Coal by Heap Leaching. Pennsylvania State University, University Park, PA, 103 pp.

Geidel, G., Carruccio, F.T., Hornberger, R., and Brady, K., Acid Drainage Technology Initiative, 2000. Guidelines and recommendations for use of kinetic tests for coal mining (AMD) prediction in the Eastern United States. In: Prediction of Water Quality at Surface Coal Mines. http://www.techtransfer.osmre.gov/nttmainsite/Library/hbmanual/predictH2O/chapter5.pdf. Retrieved September 16, 2013.

Griffiths, J.C., 1967. Scientific Method in Analysis of Sediments. McGraw-Hill, New York.

Hammarstrom, J.M., Cravotta, C.A., III, Galeone, D., Jackson, J.J., and Dulong, F., 2009. Characterization of rock samples and mineralogical controls on leachates. In: The Development and Interpretation of the ADTI-WP2 Leaching Column Method: Kinetic Test Procedure for the Prediction of Coal Mine Drainage Quality. R.J. Hornberger, and K.B.C. Brady, eds. EPA Method 1627. Office of Surface Mining Reclamation and Enforcement CT-5-30040. U.S. Department of the Interior, Washington, DC, pp. 61–111, plus appendices 5.1, 5.2, and 5.3.

Hornberger, R.J., and Brady, K.B.C., 1998. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, Kinetic (leaching) tests for the prediction of mine drainage quality. K.B.C. Brady, T. Kania, M.W. Smith, and R.J. Hornberger, eds. Pennsylvania Department of Environmental Protection, Harrisburg, PA.

Hornberger, R.J., Brady, K.B.C., Cuddeback, J.E., Telliard, W.A., Parsons, S.C., Scheetz, B.E., and Bergstresser, T.W., 2003. Development of the ADTI-WP1 (humidity cell) and ADTI-WP2 (leaching column) standard weathering procedures for coal mine drainage prediction. In: Proceedings of the 2003 SME Annual Conference.

Hornberger, R.J., Brady, K.B.C., White, W.B., Scheetz, B.E., Cuddeback, J.E., Telliard, W.A., Parsons, S.C., Loop, C.M., Bergstresser, T.W., McCracken, C.R., Jr., and Wood, D., 2004. Refinement of ADTI-WP2 standard weathering procedures, and evaluation of particle size and surface area effects upon leaching rates, Part 1; Laboratory evaluation of method performance. In: Proceedings of the 21st National

Conference, ASMR, and 25th West Virginia Surface Mine Drainage Task Force Symposium. American Society for Mining and Reclamation, Lexington, KY, pp. 916–947.

Hornberger, R.J., Brady, K.B.C., Scheetz, B.E., White, W.B., and Parson, S.C., 2005. Leaching column method for overburden analysis and prediction of weathering rates. ADTI-WP2. In: Proceedings of the 26th West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV, pp. 93–110.

Kuipers, J.R., Maest, A.S., MacHardy, K.A., and Lawson, G., 2006. Comparison of Predicted and Actual Water Quality at Hardrock Mines: The Reliability of Predictions in Environmental Impact Statements. Kuipers & Associates, Butte, MT, 228 pp.

Langmuir, D., 1997. Aqueous Environmental Geochemistry. Prentice Hall, Upper Saddle River, NJ, 600 pp.

Lasaga, A.C., 1998. Kinetic Theory in the Earth Sciences. Princeton University Press, Princeton, NJ, 811 pp.

Maest, A., Kuipers, J., Travers, C., and Atkins, D., 2005. Predicting Water Quality at Hardrock Mines: Methods and Models, Uncertainties, and State-of-the-Art. Kuipers & Associates, Butte, MT, 90 pp.

Murr, L.E., 1980. Theory and practice of copper sulfide leaching in dumps and in-situ. Minerals Science and Engineering, vol. 12, no. 3, pp. 121–189.

Murr, L.E., Cathles, L.M., Reese, D.H., Hiskey, J.B., Popp, C.J., Brierly, J.A., Boss, D., Berry, V.K., Schlitt, W.J., and Hsu, P.C., 1977. Chemical, biological and metallurgical aspects of large scale column leaching experiments for solution mining and in situ leaching. In Situ, vol. 1, no. 3, pp. 209–233.

Noll, D.A., Bergstresser, T.W., and Woodcock, J., 1988. Overburden Sampling and Testing Manual. Contract ME 86120. Pennsylvania Department of Environmental Resources, Bureau of Mining and Reclamation, Harrisburg, PA, 78 pp.

Potter, G.M., 1981. Design factors for heap leaching operations. Mining Engineering, vol. 33, pp. 277–281.

Rose, A.W., and Cravotta, C.A., III, 1998. Geochemistry of coal mine drainage. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, K.B.C. Brady, T. Kania, M.W. Smith, and R.J. Hornberger, eds. Pennsylvania Department of Environmental Protection, Harrisburg, PA, pp. 1.1–1.22.

Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L., and Ziemkiewicz, P., 1997. Neutralization potential of overburden samples containing siderite. Journal of Environmental Quality, vol. 26, pp. 673–681.

Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., Hellier, W., and Members of the Avoidance and Remediation Working Group of the Acid Drainage Technology Initiative (ADTI), 1998. A Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage. Colorado school of Mines, Dolden, CO.

Sobek, A.A., Schuller, W.A., Freeman, J.R., and Field, R.M., 1978. Laboratory Methods Applicable to Overburdens and Minesoils. EPA-600/2-78-054. U.S. EPA, Washington, DC, 203 pp.

Stumm, W., and Morgan, J.J., 1996. Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd ed. Wiley, New York, pp. 1022.

Tarantino, J.M., and Shaffer, D.J., 1998. Planning the overburden analysis. In: Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania, K.B.C. Brady, T. Kania, M.W. Smith, and R.J. Hornberger, eds. Pennsylvania Department of Environmental Protection, Harrisburg, PA, Chapter 5.

U.S. Environmental Protection Agency, 2002. Development of Test Methods for Prediction of Coal Mine Drainage Water Quality. Available from Joan Cuddeback, Computer Sciences Corporation, (703) 461–2025.

U.S. Environmental Protection Agency, 2003a. Development of Test Methods for Prediction of Coal Mine Drainage Water Quality. Available from Joan Cuddeback, Computer Sciences Corporation, (703) 461–2025.

U.S. Environmental Protection Agency, 2003b. Results of Interlaboratory Study for Evaluation of Draft ADTI-Weathering Procedure 2 (WP2): Column Test Method for Prediction of Coal Mine Drainage Water Quality. Available from Joan Cuddeback, Computer Sciences Corporation, (703) 4611– 2025.

U.S. Environmental Protection Agency, 2011. Method 1627: Kinetic Test Method for the Prediction of Mine Drainage Quality. EPA-821-R-09-002. U.S. EPA, Office of Water, Office of Science and Technology, Engineering and Analysis Division (4303T), Washington, DC, 33 pp.

White, W.B., 1986. Dissolution mechanisms of nuclear waste glasses. In: A Critical Review: Nuclear Waste Management II, D.E. Clark, W.B. White, and A.J. Machiels, eds. Advances in Ceramics, vol. 20, American Ceramic Society, Westerville, OH, pp. 431–442.

Yates, D.J.C., 1992. Physical and chemical adsorption: measurement of solid surface areas. In: Encyclopedia of Materials Characterization: Surfaces, Interfaces, Thin Films, C.R. Brundle, C.A. Evans, Jr., and S. Wilson, eds. Butterworth-Heineman, Boston, pp. 736–744.

Ziemkiewicz, P.F., Simmons, J.S., and Knox, A.S., 2003. The mine water leaching procedure: evaluating the environmental risk of backfilling mines with coal ash. In: Trace Elements in Coal Ash, K. Sajwan, ed. CRC Press, Boca Raton, FL.

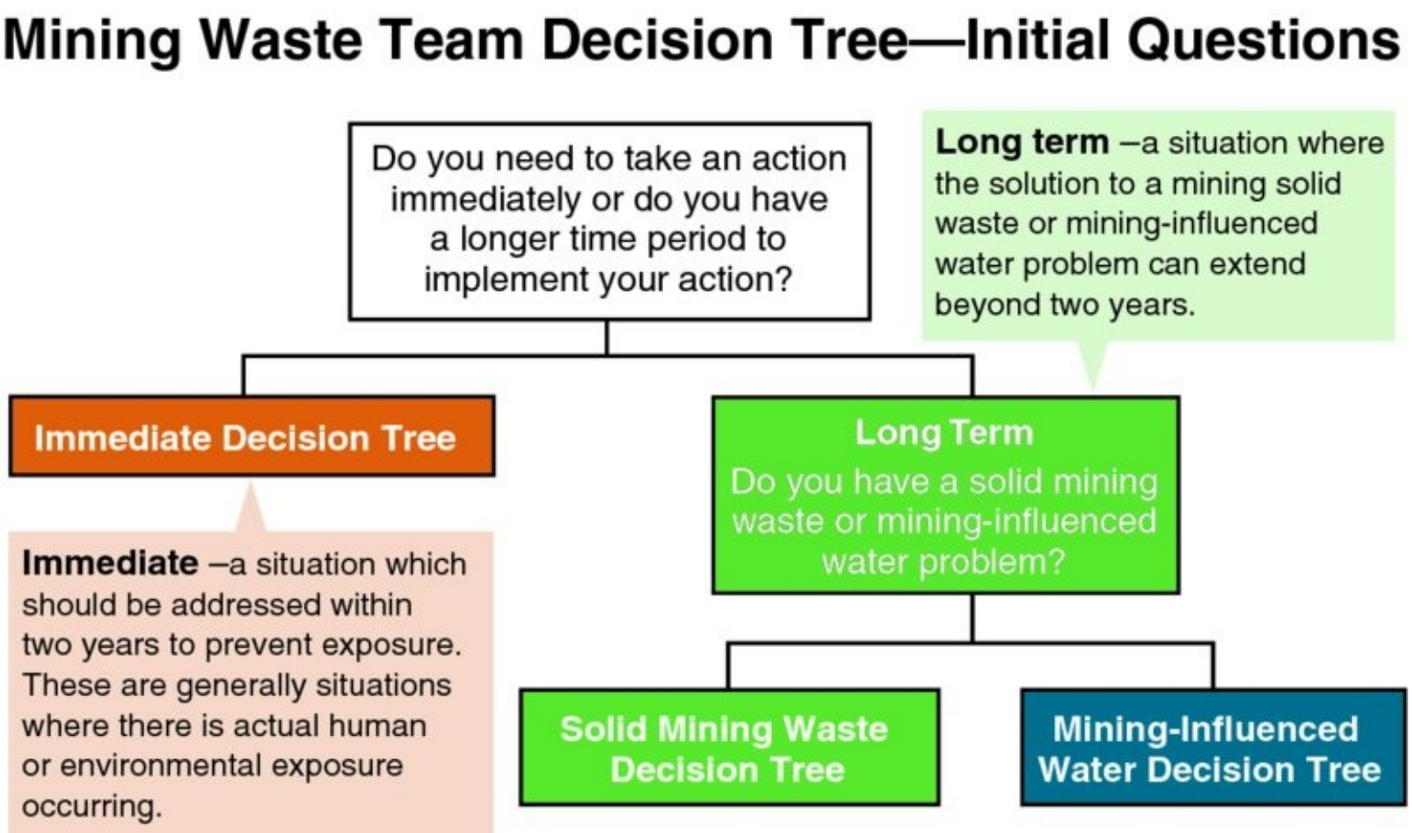
APPENDIX I
ACID MINE DRAINAGE REMEDIATION DECISION TREE

The Interstate Technology Regulatory Council (ITRC) Mining Waste Treatment Technology Section developed the Acid Mine Drainage Remediation Action Decision Tree (ITRC, 2012). The ITRC decision tree has been designed to address site-specific input to suggest a set of treatment technologies that may be useful in managing a particular mine waste site. The technologies may also be applicable to sites having acid rock drainage or acid sulfate soils. The user is presented with a series of questions relating to acid drainage issues. The user is directed toward appropriate treatment technologies based on responses to the questions. Because of the size and complexity of most mine waste sites, generally a variety of environmental challenges are to be addressed. The problems may include contaminated groundwater, contaminated residential yards, large

areas of mine waste, or contaminated surface waters. The user should go through the decision tree separately for each issue to be addressed. The ITRC website decision tree address is http://www.itrcweb.org/miningwaste-guidance/decision_tree.htm.

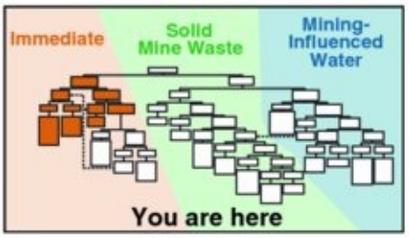
Acid Drainage Treatment Technologies

At the end of each set of questions in the decision tree is a suggested list of treatment options for addressing acid drainage. More information about the various acid drainage technologies is described on the ITRC website: http://www.itrcweb.org/miningwasteguidance/technology_overviews.htm.



Immediate Decision Tree

Part One



Immediately
Do you have a solid mining waste or mining-influenced water problem?

Solid Mining Waste
Do you need a permanent solution or will a temporary solution be sufficient?

Mining-Influenced Water
Do you need to control water quality at the receptor or at the source?

Permanent

- Excavation and Disposal
- Capping, Covers and Grading
- Passivation
- Chemical Stabilization
- Phytotechnologies
- Administrative/ Engineering Controls

Temporary

- Administrative/ Engineering Controls
- Capping, Covers and Grading
- Chemical Stabilization
- Phytotechnologies

Source

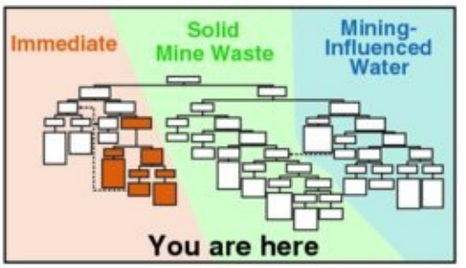
- Chemical Precipitation
- Ion Exchange
- Electrocoagulation
- or
- See Solid Mining Waste

Receptor

From Immediate Decision Tree *Part Two*

Immediate Decision Tree

Part Two



Receptor
Is the receptor of concern human or ecological?

Human Receptor

Administrative/ Engineering Controls
Pressure-Driven Membrane Separation
Ion Exchange

Ecological Receptor
Do you need a permanent solution or will a temporary solution be sufficient?

Permanent

Chemical Precipitation or See Source

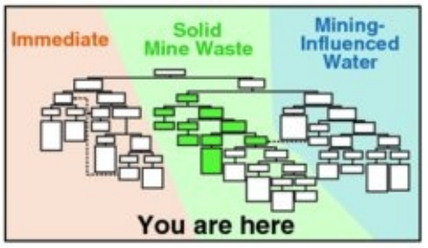
See Immediate Decision Tree *Part One*

Temporary

Administrative/ Engineering Controls
Diversionary Structures
Chemical Precipitation

Solid Mining Waste Decision Tree

Part One



Solid Mining Waste
Do you have saturated sediments affected by mine waste?

Yes

ITRC Contaminated Sediments Public Page

No
Do you need to control exposure to mining wastes which have been transported indoors?

Yes

Administrative/ Engineering Controls

No
Do you need to control exposure in a residential yard?

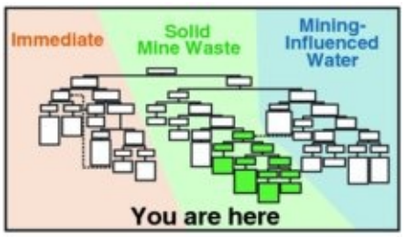
Yes

Administrative/Engineering Controls
Excavation and Disposal
Capping, Covers and Grading
Chemical Stabilization

No

Solid Mining Waste Decision Tree

Part Two



From Mining-Influenced Water Decision Tree

No
Is it feasible to remove the mine waste?

Yes

Excavation and Disposal
Subaqueous Disposal
Re-Use and Reprocess

No
Can you control exposure by treating the mining waste?

Yes

Passivation
Chemical Stabilization
In Situ Biological Treatment
Electrokinetics
Phytotechnologies

No
Can you control exposure with physical barriers?

Yes

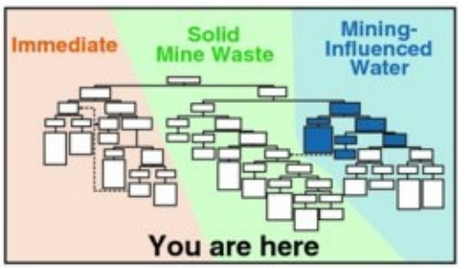
Capping, Covers and Grading
Diversionary Structures
Phytotechnologies

No

Administrative/ Engineering Controls

Mining-Influenced Water Decision Tree

Part One



Mining-Influenced Water

Do you need to control water quality at the human receptor or at the source?

Receptor

Administrative/ Engineering Controls
Pressure-Driven Membrane Separation
Ion Exchange

Source

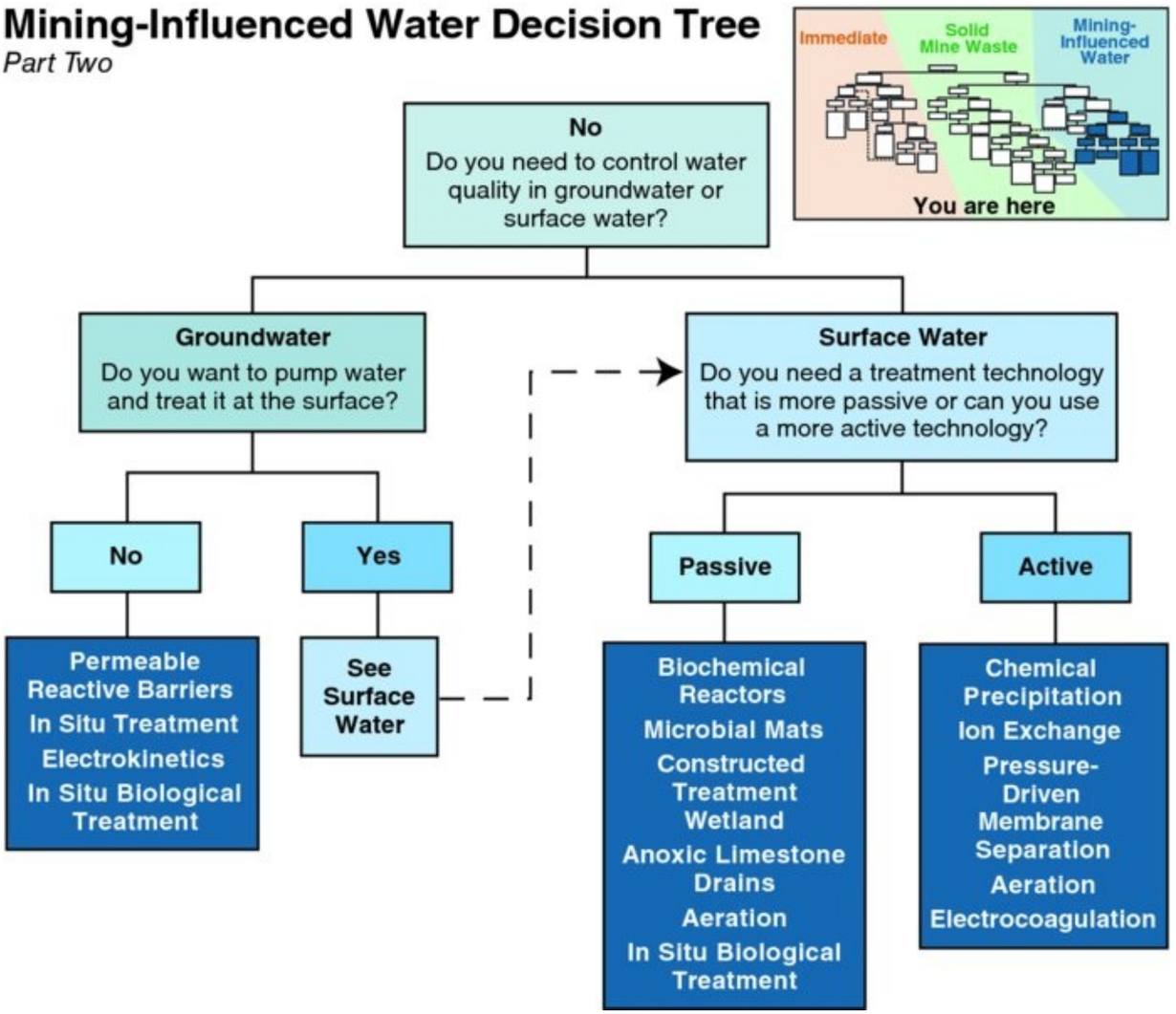
Can you eliminate the mining-influenced water by addressing the solid mining waste source?

Yes

See Solid Mining Waste Decision Tree

No

See Solid Mining Waste Decision Tree
Part Two



Reference

Interstate Technology and Regulatory Council, 2013. Decision Tree, Mining Waste Treatment Technology Section. Environmental Council of the States, Washington, DC. http://www.itrcweb.org/miningwaste-guidance/decision_tree.htm. Retrieved September 16, 2013.

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A

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