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Hydrogeochemistry and microbiology of mine drainage: An update

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ABSTRACT

The extraction of mineral resources requires access through underground workings, or open pit operations, or through drillholes for solution mining. Additionally, mineral processing can generate large quantities of waste, including mill tailings, waste rock and refinery wastes, heap leach pads, and slag. Thus, through mining and mineral processing activities, large surface areas of sulfide minerals can be exposed to oxygen, water, and microbes, resulting in accelerated oxidation of sulfide and other minerals and the potential for the generation of low-quality drainage. The oxidation of sulfide minerals in mine wastes is accelerated by microbial catalysis of the oxidation of aqueous ferrous iron and sulfide. These reactions, particularly when combined with evaporation, can lead to extremely acidic drainage and very high concentrations of dissolved constituents. Although acid mine drainage is the most prevalent and damaging environmental concern associated with mining activities, generation of saline, basic and neutral drainage containing elevated concentrations of dissolved metals, non-metals, and metalloids has recently been recognized as a potential environmental concern. Acid neutralization reactions through the dissolution of carbonate, hydroxide, and silicate minerals and formation of secondary aluminum and ferric hydroxide phases can moderate the effects of acid generation and enhance the formation of secondary hydrated iron and aluminum minerals which may lessen the concentration of dissolved metals. Numerical models provide powerful tools for assessing impacts of these reactions on water quality.

1. Introduction

1.1. General types of mine drainage

Mine drainage, i.e. waters affected by mining and mineral processing, can be acidic, circumneutral, basic, dilute, mineralized, and saline. This paper provides an overview of the wide varieties of mine water chemistry and the processes that form them. Although the main emphasis pertains to acid drainage from metal mining sites, other drainage will be mentioned including that from coal mines, diamond mines, and iron ore mines.

This review is primarily an update since the article by Nordstrom and Alpers (1999a). The same basic geochemical processes will be briefly summarized and new research will be reviewed along with topics that were not covered in the previous review.

1.1.1. Acid mine drainage and acid rock drainage

The term 'acid rock drainage' (ARD) is widely used for any acid drainage produced from rock, whether mined or not. There are numerous examples of natural acid rock drainage (NARD, see Nordstrom, 2015), acid drainage from mining activities or acid mine drainage (AMD), and acid drainage from other construction activities that must excavate sulfide-rich rock for construction of buildings, highways, bridges, and dams. Although ARD is not defined exactly in terms of pH, most ARD samples fall in the range of 2–6 and sulfate is the dominant ion. For waters with pH values of 6–9 where buffering is achieved with bicarbonate equilibria, most trace metals are insoluble and strongly sorbed. Anionic metals and metalloids (e.g. arsenate, arsenite, chromate, and molybdate) are more soluble at circumneutral to basic pH because of their negative charge. At high pH values, metals become more soluble because of their amphoteric nature. The GARD Guide chart in Fig. 1 shows the range of conditions for mine drainage. The lowest measured pH of acid mine drainage is −3.6 (Nordstrom et al., 2000). Such water is very high in dissolved constituents with a density of about 1.43 g/cm^3. There are also saline waters that are acid but that partly depends on one's definition for saline water or salinity. Some mine drainage begins circumneutral but, because of the high ferrous iron content and insufficient alkalinity, becomes acid on oxidation (Kirby and Cravotta, 2005).

1.1.2. Saline drainage

Saline waters are defined somewhat differently depending on the chosen literature source and the water type. Salinity is defined

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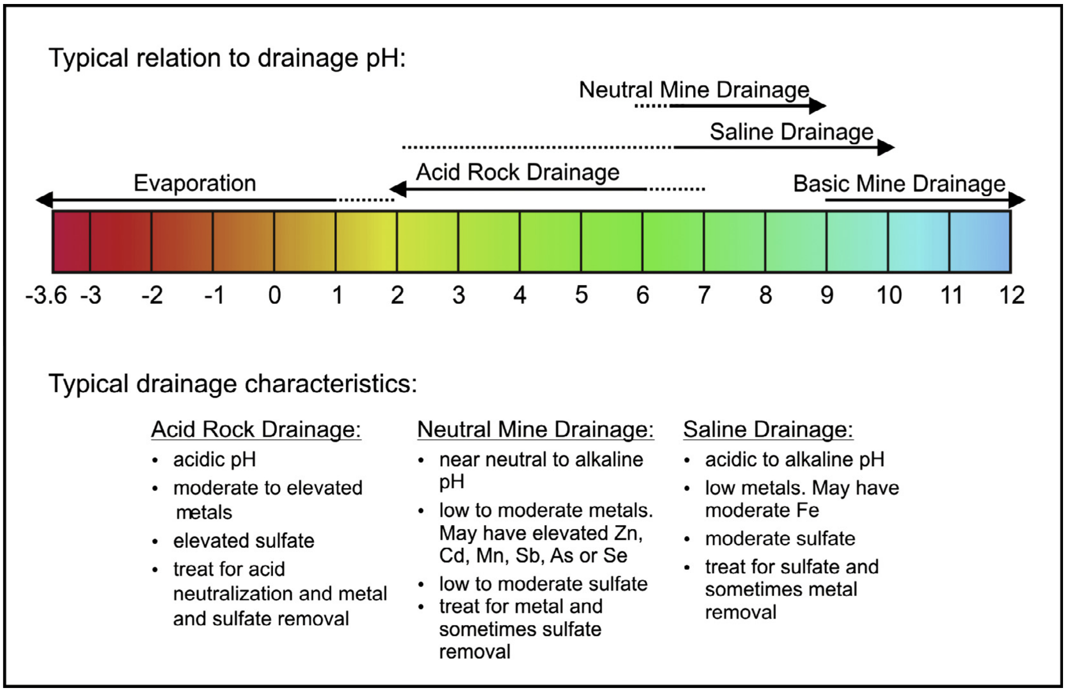

Typical drainage characteristics:

Acid Rock Drainage:

- acidic pH
- moderate to elevated metals
- elevated sulfate
- treat for acid neutralization and metal and sulfate removal

Neutral Mine Drainage:

- near neutral to alkaline pH
- low to moderate metals. May have elevated Zn, Cd, Mn, Sb, As or Se
- low to moderate sulfate
- treat for metal and sometimes sulfate removal

Saline Drainage:

- acidic to alkaline pH
- low metals. May have moderate Fe
- moderate sulfate
- treat for sulfate and sometimes metal removal

Fig. 1. Range of pH and mine drainage characteristics (modified after GARD Guide, 2009; http://www.gardguide.com/).

by oceanographers in reference to seawater, its dilution along coastal margins, and its concentration by evaporation. Its definition is based on either chlorinity or conductivity (Millero, 2001). Salinity is also defined more generally as the amount of dissolved solids in water. A classification system was suggested by Gorrell (1958) based on sodium chloride concentration, modified in a more general way to total dissolved solids by Davis and De Wiest (1966), and modified again by Kharaka and Hanor (2003) which is reproduced in Table 1.

The cutoff between saline water and brine was changed by Kharaka and Hanor (2003) to be the salinity of seawater, 35,000 mg/L, a useful reference value. A saline water is also considered in a general way to be any water with more than 10,000 mg/L dissolved solids up to seawater.

Using this classification scheme (Table 1), most ARD would be brackish water, the next most abundant would be saline, and a smaller number would qualify for either freshwater or brine. However, sodium chloride is rarely a major component of mine waters. Mines near the coast that have seawater intrusion and mines that are located in mid-continent areas in the vicinity of dissolving evaporite deposits or bitterns (residual brines after evaporites have formed) commonly have high sodium chloride content. In the present discussion, we are concerned with sodium chloride salinity in addition to the salinity developed from pyrite oxidation and acid dissolution of the host rock. These waters are not limited to mines where salt water intrusion or dissolution of evaporate minerals occurs. Indeed, brackish, saline water, or brine may be encountered underlying fresh groundwater virtually everywhere if one goes deep enough. In some mines located far from the ocean, vugs have been discovered that contained brines dominated by sodium-calcium-chloride (Guha and Kanwar, 1987). In other areas a brackish mine water with a similar chemical signature but with a distinctly non-seawater Br/Cl ratio was thought to be derived from fluid inclusions (Nordstrom et al., 1989). Likewise, discharges from underground coal mines have been documented with elevated concentrations of alkali and halogen elements and non-seawater Br/Cl ratio which could be attributed to connate waters and residual salts in sedimentary rocks and mixing of freshwater and brines from deep-lying oil and gas-bearing formations (Cravotta, 2008a, 2008b).

As an example of saline mine drainage, Cornish tin mine waters have been found to contain from 90 to 19,300 mg/L total dissolved solids (Edmunds et al., 1984, 1987). The increased salinity is caused by sodium–calcium-chloride type water that is thought to originate from fluid reactions with the rock. Seawater is discounted, even though the Br/Cl ratios are exactly those of seawater, because of the water isotope composition. However, seawater intrusion is still a viable hypothesis in addition to rock-derived salinity. The pH values range from 3.5 to 8.35 and temperatures ranged from 15 to 44 °C. Sulfate concentrations are less than typical seawater values (<2700 mg/L; Millero, 2001) and generally increase with lower pH values consistent with pyrite oxidation. Two examples of mine waters reflecting the range of chemical composition are shown in Table 2.

Table 1
Classification of waters by salinity (Kharaka and Hanor, 2003).

Name	Concentration range, mg/L
Freshwater	<1,000
Brackish water	1,000–10,000
Saline water	10,000–35,000
Brine	>35,000

1.1.3. Neutral mine drainage

Neutral mine drainage refers to drainage waters with pH values ranging between 6 and 9 that contain other dissolved constituents, principally SO_4^{2-} and dissolved metals derived from sulfide oxidation. Neutral mine drainage occurs in settings where the acid consumption associated with carbonate-derived neutralization capacity is sufficient to maintain neutral pH conditions. Neutral drainage is generally observed at sites where the acid neutralization capacity associated with carbonate mineral content is greater than the acid generation potential associated with the sulfide content. In these settings, neutral pH conditions will be maintained

Table 2
Example of an acid brackish low-chloride mine water and a circumneutral saline mine water from Cornwall tin mines (Edmunds et al., 1984, 1987).

Constituent (mg/L except where noted)	Wheal Jane	South Crofty
Temperature, °C	21.6	41.5
pH, standard units	3.5	7.21
HCO$_3$	–	64
Cl	179	12,000
SO$_4$	1,390	173
F	4.4	2.70
Ca	191	2,325
Mg	43	72.8
Sr	1.87	41.2
Na	93	4,440
K	12.0	135
Li	2.7	120
SiO$_2$	25.5	35.3
Fe	346	4.75
Mn	19.7	5.00
Ni	0.86	0.210
Cu	<0.008	0.022
Co	0.27	–
As	2.1	–
Be	0.150	–
Zn	125	–

throughout the duration of acid generation (e.g., Blowes, 1990; Kirby and Cravotta, 2005; Lindsay, 2009; Lindsay et al., 2009; Church et al., 2007; Table 3). Neutral drainage is also observed in the early stages of the weathering of mine wastes with an acid generation capacity in excess of the carbonate-based neutralization capacity (Jurjovec et al., 2002). At these locations, neutral pH conditions will continue until the carbonate mineral content is depleted to the extent that the rate of acid consumption no longer exceeds the rate of acid generation. The neutral pH period prior to the onset of acid generation is referred to as the lag period and may extend for a few months to many years. Some waters, like the third analysis in Table 3, contains potential acidity from the presence of high concentrations of dissolved, reduced iron. Indeed, this water becomes acidic downstream from oxidation, hydrolysis, and precipitation of iron.

1.1.4. Basic mine drainage

Occasionally mine water has been found to have pH values above 9. The circumstances that can lead to such water compositions include (1) low permeability rock with abundant feldspars that can react in a closed system, exchange of protons for alkalis with removal of bicarbonate through calcite precipitation (Nordstrom et al., 1989), (2) evolution of groundwater to a sodium bicarbonate type through ion exchange, sulfate reduction, and organic carbon oxidation (Cederstrom, 1946; Thorstenson et al., 1979; Chapelle, 2000), (3) dissolution of altered marls that contained lime (Khoury et al., 1985), and (4) dissolution of villiaumite (NaF) with evaporation (NaF; Kraynov et al., 1969). Three examples of basic mine waters are reproduced in Table 4. The first is from a coal mine in South Africa (Azzie, 2002), the second is from the Stripa iron ore mine in Sweden (Nordstrom et al., 1989) and the third is from the Lovozero mine in the Kola Peninsula (Kraynov et al., 1969).

2. Mineralogy

The primary source of most AMD problems arises from the oxidation of iron sulfide minerals and subsequent release of acidity, sulfate, and dissolved metals. Although acid generation and metal release are usually associated with the oxidative dissolution of sulfide minerals, other mineral groups also can contribute metals such as sulfates, carbonates, oxides, and aluminosilicates. Blowes and Jambor (1990) describe a classification scheme to distinguish minerals in their chemically unaltered state from those that had been affected by weathering within mine workings and mine wastes, and from those that had been affected by sample collection, storage, and handling.

Table 3
Examples of three circumneutral mine drainage waters.

Constituent (mg/L except where noted)	Delnite mine tailings impoundment unsaturated zone pore water, ON, Canada[a]	Greens Creek tailings impoundment unsaturated zone pore water, AK, USA[b]	Silver Ledge Mine, San Juan Mountains, CO, USA[c]
T, °C	7.0	9.2	5.6
pH	7.42	7.66	5.70
Specific conductance, μS/cm	1,020	n.d.	1,090
Constituent			
SO$_4$	1,910	2,620	518
Cl	2.56	1.3	n.d.
F	<0.1	n.d.	n.d.
Alkalinity, (as CaCO$_3$)	120	90	30
SiO$_2$	5.34	n.d.	27.4
Na	7.02	<15	3.93
K	5.81	9.6	n.d.
Ca	199	518	211
Mg	366	318	8.99
Fe^{II}	n.d.	n.d.	11.8
Fe$_{(T)}$	1.04	0.54	12.3
Al	<1	<0.25	0.879
Mn	0.22	0.97	2.43
Cu	<0.01	<0.001	0.011
Pb	0.12	<0.001	<0.001
Zn	0.07	0.88	0.701
Cd	<0.001	<0.002	0.0063
Ni	<0.04	0.038	<0.020
Co	<0.05	<0.005	n.d.
Cr	<0.05	0.0026	<0.015

[a] 4 m below ground surface (Blowes, 1990).
[b] 1.25 m below ground surface (Lindsay, 2009).
[c] Near portal entrance (Church et al., 2007).

Table 4
Examples of chemical composition of three basic mine waters.

Constituent (mg/L except where noted)	Underground CMD, Vryheid Formation, South Africa	Stripa mine water, Sweden	Mine water from Lovozero Massif
T, °C	n.d.	8.6	n.d.
pH	9.03	10.06	11.74
Specific Conductance, µS/cm	2,070	1,090	n.d.
Constituent			
SO_4	376	57	n.d.
Cl	196	460	75
F	0.34	5.3	11,000
HCO_3	311	18	2,666
SiO_2	2.52	18	9,000–13,000
Na	235	218	24,038
K	26.4	0.44	222
Ca	71.2	94	n.d.
Mg	74.6	0.03	100
Fe^{II}	<0.001	0.0007	n.d.
$Fe_{(T)}$	0.437	0.004	n.d.
Al	0.022	0.024	n.d.
Mn	0.003	<0.001	n.d.
Cu	<0.001	0.007	0.283
Pb	n.d.	<0.01	0.032
Zn	0.001	<0.002	n.d.
Cd	n.d.	n.d.	n.d.
Ni	<0.001	<0.001	n.d.
Co	<0.001	<0.005	n.d.
Cr	<0.001	<0.001	n.d.

i. *Primary minerals:* refers to those minerals initially present in the ore and gangue mineral assemblages. These minerals include the sulfide minerals initially present in the orebody, sulfide, (oxy)hydroxide and hydroxysulfate minerals associated with supergene enrichment, and the silicate and carbonate gangue minerals associated with the ore body.
ii. *Secondary minerals:* include those minerals that form in mine workings or mine wastes. Secondary minerals are usually derived from oxidation reactions within the mine wastes, and include sulfate minerals such as gypsum, Fe(III) (oxy)hydroxide minerals, including goethite and hydroxysulfate phases, such as jarosite.
iii. *Tertiary minerals:* are those minerals that form after samples have been extracted from the mine workings or from the mine wastes. Tertiary minerals are typically Ca, Mg and Fe(II) sulfates, but may also include iron (oxy)hydroxides and sulfides such as covellite.
iv. *Quaternary minerals:* are those minerals that form during storage of dried samples. These minerals are typically hydrated iron sulfate minerals, such as rozenite or siderotil, and may also occur as secondary or tertiary minerals as well.

2.1. Primary sulfides, sulfates, and supergene enrichment

The iron sulfide minerals, pyrite and pyrrhotite, are the minerals most commonly implicated in the generation of AMD. The oxidation of these minerals results in the release of SO_4^{2-}, Fe^{2+}, and H^+. Further oxidation of Fe^{2+} and precipitation of Fe(III) oxy(hydroxides) and hydroxysulfates result in generation of additional acidity. Substitution of trace elements in the pyrite and pyrrhotite structure can result in the release of high concentrations of these elements to solution. For example, the occurrence of elevated concentrations of Ni and Co in drainage water from waste rock at the Diavik Diamond Mine has been attributed to the oxidation of Ni- and Co-bearing pyrrhotite (Smith et al., 2013). In addition to pyrite and pyrrhotite, trace element-bearing sulfide minerals, commonly present in ore deposits and mine wastes can contribute to acid generation, and more importantly, release toxic dissolved constituents, such as As, Cd, Cu, Mo, Ni, Pb, and Zn, to mine drainage waters. For example, the oxidation of the pyrite-rich sulfide mineral assembly in the tailings impoundment at the Waite Amulet mine site (Rouyn-Noranda, QC) resulted in the generation of acidic pore water containing high concentrations of Cu, Zn, Pb, and Ni (Blowes and Jambor, 1990). Oxidation of pyrite and arsenopyrite contained in the carbonate-rich tailings at the Delnite mine site resulted in neutral pH pore water containing low concentrations of dissolved Fe (typically <10 mg L^{-1}), high concentrations of SO_4^{2-} (2,500–4,500 mg L^{-1}), and high concentrations of dissolved As (up to 45 mg L^{-1}).

2.2. Sulfate minerals

Sulfate minerals associated with mine workings and mine wastes may provide a source of acidity, sulfate, and dissolved metals to mine drainage. The most dramatic example of the potential for release of dissolved constituents is the occurrence of the complex suite of secondary sulfate minerals observed at the Iron Mountain mine, CA (Nordstrom and Alpers, 1999b; Nordstrom et al., 2000). Extensive sulfide oxidation released high concentrations of SO_4^{2-}, Fe, and other metals to the mine waters. Further enrichment by evapoconcentration resulted in the development of highly acidic waters, with pH values as low as −3.6 and the formation of a series of secondary sulfate minerals ranging from melanterite, a hydrated ferrous sulfate mineral, to rhomboclase, an H^+-containing Fe(III) hydroxysulfate mineral (Alpers et al., 2000). Controlled dissolution experiments conducted with samples from the Iron Mountain site indicate the potential for prolonged release of acidic water in the absence of on-going sulfide oxidation.

Other, less dramatic, examples of the impacts of sulfate mineral dissolution have been observed. Al et al. (1994) characterized tailings derived from the Kidd Creek metallurgical site. At Kidd Creek sulfide-bearing tailings are co-disposed with the residues derived from the jarosite precipitation process used at the Kidd Creek Zn refinery. In addition to jarosite, these residues contain gypsum and iron oxyhydroxides. Co-disposal of the jarosite residue and the sulfide-bearing concentrator tailings results in the reductive dissolution of the jarositic wastes, leading to a decline in the pore-water pH and increased concentrations of dissolved SO_4^{2-}, Fe, Zn, and other metals (Al et al., 1994). In a recent study of an in situ remediation system, Lindsay et al. (2011) observed increased concentrations of dissolved Ba within the sulfate-reducing zone of a tailings impoundment. This increase was attributed to the dissolution of barite enhanced by removal of sulfate *via* bacterially mediated sulfate reduction.

3. Geochemical and microbiological processes

3.1. Aqueous iron oxidation

The oxidation of dissolved Fe^{2+} to Fe^{3+} is a key to understanding the oxidation of sulfide minerals because Fe^{3+} is a more effective oxidant than oxygen. Oxidation of Fe^{2+} is a more complex process than it might seem. The oxidation rates change by orders of magnitude depending on pH and the presence or absence of iron-oxidizing microbes, nutrient availability for iron-oxidizers, hydrolysis of dissolved ferric iron, polymerization of ferric iron, and precipitation. Phases that can precipitate include schwertmannite, goethite, ferrihydrite, lepidocrocite, and jarosite. Usually a mixture precipitates under field conditions but laboratory and field studies have shown that ferrihydrite tends to dominate at pH values >5.5, jarosite tends to dominate at pH 0.8–2.5, and schwertmannite tends

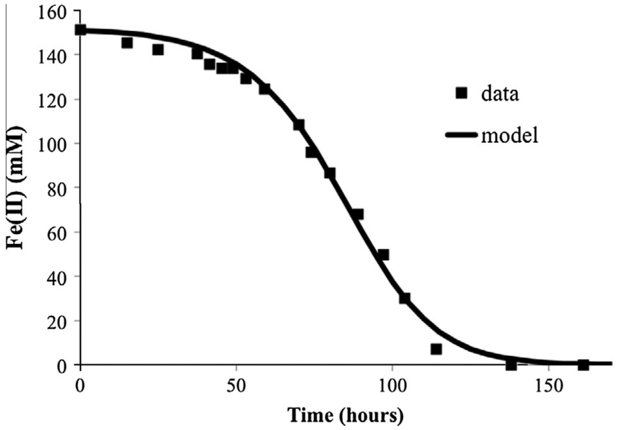

Fig. 2. Typical Fe^{2+} oxidation curve as a function of time (Nordstrom and Campbell, 2014).

to dominate at intermediate pH values (Alpers et al., 1989; Bigham and Nordstrom, 2000). Although schwertmannite can be precipitated as a pure phase in the laboratory, it converts to goethite at the intermediate to higher pH values (2.5–5.5; Bigham et al., 1996; Regenspurg et al., 2004; Schwertmann and Carlson, 2005) and to jarosite at lower pH values (Wang et al., 2006).

The following figures demonstrate the complexity of iron oxidation. The usual plot of Fe^{2+} decreasing with time by iron-oxidizing microbes is shown in Fig. 2 (Nordstrom and Campbell, 2014). The sigmoidal shape of the curve reflects the microbial growth from lag phase through exponential growth (zero-order rate) to exponential decay as the energy source becomes vanishingly small (Lundgren et al., 1964; Nordstrom, 2003). The curve can be fit with the standard Monod kinetic equation (Monod, 1949; Nordstrom and Campbell, 2014).

In Fig. 3, Liao et al. (2009) allowed Fe^{2+} to oxidize in 9 K medium (Silverman and Lundgren, 1959) at 26 °C, over a range of pH values from 1.4 to 2.4 and plotted the change in pH during the oxidation. As the initial pH of each run is taken an increment higher, there developed a peak in the pH. The rise in pH occurs because the oxidation of Fe^{2+} consumes protons:

$$Fe^{2+}_{(aq)} + 1/4O_{2(g)} + H^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 1/2H_2O_{(l)} \tag{1}$$

After a delay, the Fe^{3+} hydrolyses and decreases the pH:

$$Fe^{3+}_{(aq)} + H_2O_{(l)} \rightarrow Fe(OH)^{2+}_{(aq)} + H^{+}_{(aq)} \tag{2}$$

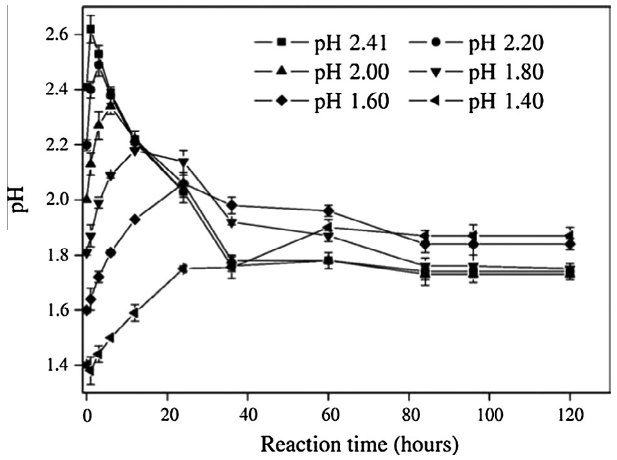

Fig. 3. Change in pH during the oxidation of Fe^{2+} in 9 K medium at 26 °C (Liao et al., 2009).

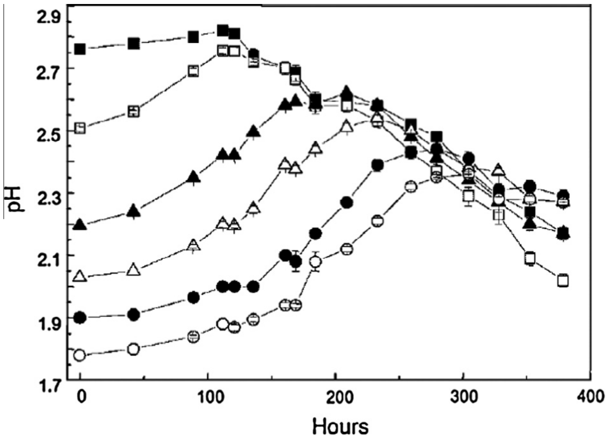

Fig. 4. Change in pH during oxidation of 9 K medium at 5 °C with initial pH designated by different symbols (○, pH 1.8; ●, pH 1.9; △, pH 2.0; ▲, pH 2.2; □, pH 2.5; ■, pH 2.8; from Kupka et al., 2007 with permission).

Finally, the hydrolyzing iron precipitates as a mineral phase and further decreases the pH and approaches an equilibrium state:

$$Fe(OH)^{2+}_{(aq)} + H_2O_{(l)} \rightarrow FeOOH_{(goethite)} + 2H^{+}_{(aq)} \tag{3}$$

At higher initial pH values the peak sharpens and moves closer to the initial onset of oxidation and eventually disappears because the Fe^{3+} hydrolyzes more rapidly at higher pH values and the pH increase from oxidation (Eq. (1)) cannot be distinguished from hydrolysis (Eq. (2)). This increase in hydrolysis rate is related to the difference in initial pH from the pH equivalent of the first hydrolysis constant for Fe^{3+}, pK = 2.2. This effect can be seen in the data from Kupka et al. (2007) (Fig. 4) which was an iron oxidation study with 9 K medium carried out at low temperature (5 °C). The lower temperature would also slow the rate of microbial growth so that the peaks in the pH curves would take longer to obtain. In both studies the rate of iron oxidation also seems to slow with lower initial pH.

In Fig. 5, the initial rate (or the lag phase) is enhanced by the presence of iron precipitates (primarily a mixture of schwertmannite and goethite). If more ferrous iron is added to a solution

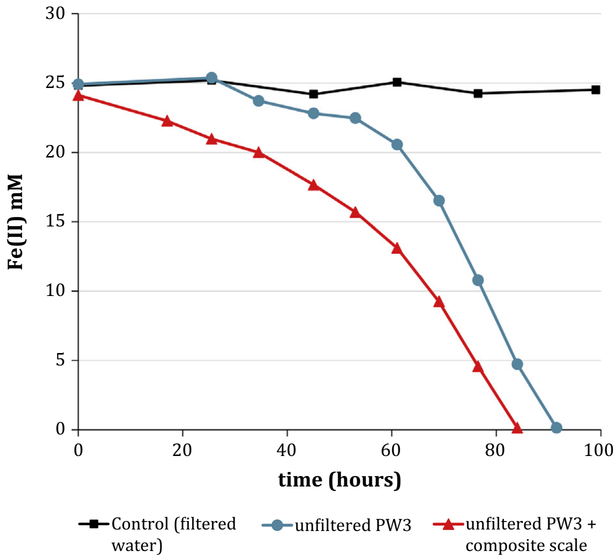

Fig. 5. Oxidation of aqueous Fe^{2+} for an unfiltered mine portal water sample from Iron Mountain, California (PW3) by itself and another with an iron precipitate (composite scale) added that originated from the same water (Campbell et al., 2013).

similar to this when the Fe^{2+} has gone to zero, the oxidation of Fe^{2+} is immediate without any lag phase (Nordstrom, 1985).

Research continues on the rates of Fe^{2+} oxidation because it is the main control on the rate of pyrite oxidation. This rate is microbially mediated at low pH values and as much as six orders of magnitude faster than the abiotic rate (Nordstrom, 2003). Research also continues on Fe^{2+} oxidation rates in circumneutral mine waters, where microbial catalysis is relatively unimportant. Slightly acidic pH (~6) of most such mine waters tends to limit the rate of Fe^{2+} oxidation. Aeration downstream of the mine water outfall or within a treatment system promotes outgassing of CO_2, which results in increased pH and increased rates of Fe oxidation in accordance with abiotic rate laws (Kirby et al., 2009; Cravotta, 2015).

3.2. Aqueous arsenic and antimony oxidation

Arsenic and antimony solubilities and mobilities in natural waters are highly dependent on their redox state as well as on pH. Arsenic (III) is quite soluble and poorly sorbed. Under conditions of high sulfide and moderately acidic pH (3–4), As(III) will precipitate as an arsenic sulfide phase. Arsenic (V) sorbs more strongly than As(III) and forms insoluble precipitates such as scorodite, an Fe(III)-arsenate. Antimony (V) also tends to be more soluble when reduced to Sb(III) but behaves differently from As. Hence, the oxidation and reduction rates of As and Sb are essential to understanding their mobilities, toxicities, and environmental risks.

3.2.1. Aqueous arsenic oxidation

Oxidation of arsenite, $As^{III}O_3$, to arsenate, $As^{V}O_4$, using oxygen as the oxidant will lower a circumneutral pH solution according to the reaction:

$$2H_3AsO_3 + O_2 \rightarrow HAsO_4^{2-} + H_2AsO_4^- + 3H^+ \tag{4}$$

The amount of pH decrease depends on the amount of arsenite oxidized and the amount of other buffers present, but for every two moles of arsenite oxidized three moles of protons will be produced. Gmelins (1908) cited publications from the early part of the 19th century demonstrating that reduction and oxidation of dissolved arsenic is very slow unless a strong reductant or strong oxidant are present. Gosio (1897), Green (1918), and Green and Kestell (1919) recognized that microbes were also catalysts for arsenic oxidation or arsenic reduction. Hence, oxidation rates of aqueous arsenic are very slow abiotically, about 1×10^{-5} $\mu mol\,L^{-1}\,h^{-1}$ or about seven orders of magnitude slower than the microbial rate (McCleskey et al., 2004; Nordstrom, 2003). Asta et al. (2012) reported microbial arsenic oxidation rates during exponential growth of 15–78 $\mu mol\,L^{-1}\,h^{-1}$ for circumneutral water (temperatures from 4 °C to ambient) from underground in the Giant Mine, Yellowknife, Northwest Territories, Canada which compares quite favorably with the data of Gihring and Banfield (2001) and Gihring et al. (2001) of 68–73 $\mu mol\,L^{-1}\,h^{-1}$ based on 70 °C lab and field oxidation with *Thermus* species from Yellowstone National Park, Lassen National Park, and standard cultures.

3.2.2. Aqueous antimony oxidation

Antimonite oxidation to antimonate has a slightly smaller effect on pH because of a difference in the hydrolysis product of antimonate ion, according to the reaction:

$$H_3SbO_3 + 1/2O_2 + 2H_2O \rightarrow Sb(OH)_6^- + H^+ \tag{5}$$

One mole of hydrogen ion is produced for every mole of antimonite ion oxidized at near neutral pH.

Very few rates of aqueous antimony oxidation have been reported. The same generalization applies to reduction and oxidation as with arsenic, i.e. it is very difficult to oxidize or reduce dissolved antimony unless strong reagents are used or unless microbial catalysis occurs. Lehr et al. (2007) studied the oxidation of antimonite by *Agrobacterium tumefaciens* and by a thermoacidophilic alga (order *Cyanidales*) from Norris Geyser Basin in Yellowstone National Park. From their rate curves we estimate a rate of 0.4 $\mu mol\,L^{-1}\,h^{-1}$ for the bacterium and 0.2 $\mu mol\,L^{-1}\,h^{-1}$ for the eukaryote. Asta et al. (2012) measured rates of antimony oxidation at neutral and acidic pH values, at two different temperatures, and with and without microbial communities. The results were similar for different pH values and different temperatures, 0.01–0.05 $\mu mol\,L^{-1}\,h^{-1}$ with microbes present or with Fe(III) present at low pH. Aqueous antimony oxidation rates are two to three orders of magnitude slower than aqueous arsenic oxidation rates.

3.3. Sulfide mineral oxidation

3.3.1. Pyrite oxidation

Pyrite, the most abundant sulfide mineral in the Earth's crust, is commonly associated with coal, base metal, and gold deposits. Oxidation of sulfide minerals has been the focus of extensive study because of its importance in environmental management and metallurgical processing. Reviews of sulfide mineral oxidation and the formation of acid mine drainage are given by Nordstrom and Alpers (1999a), Rimstidt and Vaughan (2003), Rosso and Vaughan (2006), and Blowes et al. (2013).

Pyrite oxidation can proceed through chemical, biological, and electrochemical pathways, in oxic and anoxic systems, when mineral surfaces are exposed to water and an oxidant (including O_2, or Fe^{3+}, or mineral catalysts, e.g., MnO_2). Oxidation of pyrite by atmospheric oxygen produces one mole of Fe^{2+}, two moles of SO_4^{2-} and two moles of H^+ for every mole of pyrite oxidized (Nordstrom, 1982):

$$FeS_2(s) + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{6}$$

The Fe(II) thus released may be oxidized to Fe(III) (Eq. (1)). Precipitates of Fe(III) oxyhydroxides, such as goethite (α-FeOOH) and ferrihydrite (nominally $5Fe_2O_3{\cdot}9H_2O$), may form (Eq. (3)). Adding Eqs. (1), (2), (3) and (6) yields the overall reaction:

$$FeS_2(s) + 15/4O_{2(aq)} + 5/2H_2O_{(aq)} \rightarrow 2SO_4^{2-} + FeOOH_{(s)} + 4H^+_{(aq)} \tag{7}$$

This overall reaction results in the release of 4 mol of H^+ for each mole of pyrite oxidized.

3.3.1.1. Chemical oxidation by Fe^{3+} and O_2. The oxidation of pyrite commences with the adsorption of O_2 and H_2O by bonding to Fe^{2+} to the variably protonated pyrite surface. Under acidic (pH <4) and oxygenated conditions, the principal oxidation products are Fe(III) hydroxysulfates (Todd et al., 2003), predominantly schwertmannite for pH 2–4 and predominantly jarosite for lower pH values. Under higher pH conditions, a mixture of Fe(III) oxyhydroxide and hydroxysulfate phases are observed. Under alkaline conditions, goethite becomes the predominant secondary phase on pyrite surfaces.

Under acidic conditions, the major oxidant of pyrite is Fe^{3+} (Singer and Stumm, 1970). Pyrite oxidation by Fe^{3+} at circumneutral pH has also been observed (Brown and Jurinak, 1989; Moses et al., 1987), but the reaction is limited by the low aqueous Fe^{3+} concentrations at neutral pH.

Williamson and Rimstidt (1994) developed a rate law for the oxidation of pyrite by O_2 that covers a broad range of O_2 concentrations over a pH range of 2–10:

$$R = 10^{-8.19(\pm 0.04)} \frac{m_{DO}^{0.5(\pm 0.04)}}{m_{H^+}^{0.11(\pm 0.01)}} \tag{8}$$

where R is the rate of pyrite dissolution in units of $mol\,m^{-2}\,s^{-1}$.

Williamson and Rimstidt (1994) also formulated rate laws describing pyrite oxidation by Fe^{3+} in the presence of varying concentrations of Fe^{2+}, under fixed concentrations of O_2, over a pH range of 0.5–3.0:

$$R = 10^{-6.07(\pm0.57)} \frac{m_{Fe^{3+}}^{0.93(\pm0.07)}}{m_{Fe^{2+}}^{0.40(\pm0.06)}} \tag{9}$$

where R is the rate of pyrite dissolution in units of mol m^{-2} s^{-1}.

Activation energy values determined for pyrite oxidation range from 50 kJ mol^{-1} for pH 2–4 to 92 kJ mol^{-1} for pH 6–8, regardless of whether dissolved O_2 or Fe(III) is used as the oxidant (Nicholson, 1994; Wiersma and Rimstidt, 1984). The high activation energies observed suggest that the rate-limiting step in pyrite oxidation is related to electron transfer at the pyrite surface.

Holmes and Crundwell (2000) used measurements of the kinetics of pyrite oxidation and reduction to derive expressions for the mixed potential and rate of dissolution, which agreed with those obtained by McKibben and Barnes (1986) and Williamson and Rimstidt (1994). The results showed that a series of electrochemical reaction steps, occurring at the mineral–solution interface, control the rate of dissolution. These steps are (1) cathodic reaction transferring electrons from the pyrite surface to the aqueous oxidant species, (2) electron transport from the anodic to cathodic site, and (3) anodic reaction involving H_2O molecules interacting with S atoms to form a sulfoxy species (Rimstidt and Vaughan, 2003).

The rate of pyrite oxidation is limited by the transport of reactants to the pyrite surface under neutral pH values due to the presence of secondary Fe(III) oxyhydroxide coatings. These coatings can develop in two stages: the initial precipitation of Fe(III) oxyhydroxide colloids and their attachment to pyrite surfaces, followed by infilling of additional Fe(III) oxyhydroxide particles within the initial coating (Huminicki and Rimstidt, 2009). The transport of reactants to pyrite surfaces is limited by both of these Fe(III) oxyhydroxide accumulation processes.

3.3.2. Pyrrhotite oxidation

Pyrrhotite is the second most common Fe-sulfide mineral. Several studies have focused on pyrrhotite oxidation (e.g. Buckley and Woods, 1985; Thomas et al., 1998; Janzen et al., 2000). Pyrrhotite occurs in both monoclinic and hexagonal forms. The disordered hexagonal close-packing structure of pyrrhotite (i.e., NiAs-type structure), results in both stoichiometric and nonstoichiometric ($Fe_{1-x}S$) compositions, in which x can vary from 0.125 (Fe_7S_8) to 0 (FeS). Reaction rate studies indicate the hexagonal pyrrhotite form is slightly more reactive (Orlova et al., 1988), with activation energies of 46 kJ mol^{-1} reported for the hexagonal variety and 50 kJ mol^{-1} for the monoclinic structure. Janzen et al. (2000) did not observe a consistent trend between activation energy and crystal structure. Nicholson and Scharer (1994) observed that the oxidation rate is dependent on pH, with reported activation energies ranging from 52 to 58 kJ mol^{-1} at pH 2–4, and increasing to 100 kJ mol^{-1} at pH 6. This range in activation energies is similar to values observed for pyrite, suggesting the reaction rate is surface controlled.

3.3.2.1. Chemical oxidation by O_2 and Fe^{3+}. Dissolution of pyrrhotite can proceed by pathways that are oxidative or non-oxidative. The oxidative pathway can proceed up to 1000 times more slowly than non-oxidative dissolution (Thomas et al., 1998). Both dissolved O_2 and Fe^{3+} can oxidize pyrrhotite. The overall reaction for oxidation of pyrrhotite by O_2 is:

$$Fe_{1-x}S + \left(2 - \frac{1}{2}x\right)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+ \tag{10}$$

or for the end member where $x = 0$:

$$FeS + 2O_2 \rightarrow Fe^{2+} + SO_4^{2-} \tag{11}$$

In this reaction, the release of H^+ is dependent on pyrrhotite stoichiometry, with a maximum of one-quarter mole of H^+ released from the oxidation of one mole of the Fe-deficient form ($x = 0.125$). In contrast, no H^+ is released during the oxidation of troilite, the stoichiometric form ($x = 0$). Additional H^+ are released by the combined oxidation of Fe(II) (Eq. (2)) and subsequent precipitation of ferric (oxy)hydroxides (Eq. (3)).

Partial oxidation of pyrrhotite is common and may result in transformation of only a portion of the S to sulfate, with the remaining S accumulating as partially oxidized sulfur species, including polysulfides and elemental sulfur (Janzen et al., 2000).

$$\begin{aligned} Fe_{1-x}S_{(s)} &+ \left(\frac{1-x}{2}\right)O_2 + 2(1-x)H^+ \\ &\rightarrow (1-x)Fe^{2+} + S_x^{n<0} + (1-x)H_2O \end{aligned} \tag{12}$$

Oxidation of pyrrhotite proceeds at rates that are 20–100 times faster than pyrite at 25 °C.

3.3.2.2. Non-oxidative mechanism. Non-oxidative dissolution of pyrrhotite is observed under acidic conditions (Ostwald, 1902):

$$FeS + 2H^+ \rightarrow Fe^{2+} + H_2S \tag{13}$$

a characteristic of acid dissolution of monosulfide minerals.

Thomas et al. (1998, 2001) proposed a two-pathway dissolution mechanism: (1) Fe^{2+} is released from the surface with no release of electrons from the structure, and (2) reduction of polysulfide to sulfide following a critical accumulation of charge, resulting in the release of negative charge from the surface in the form of HS^-.

3.3.3. Advances in AMD microbiology

Research and reviews in AMD microbiology have continued to advance our understanding of dominant microbial processes in mine environments that promote toxic metal mobility and attenuation (Baker and Banfield, 2003; Schippers et al., 2010; Johnson, 2012) and for applications in hydrometallurgy and metals recovery (Hallberg, 2010; Rawlings, 2002). Schippers et al. (2010) compiled more than 70 microbiological studies of sulfidic mine wastes and heap leach piles. Robbins (2000) reported 86 genera or species that live in waters with pH <4.5. Baker and Banfield (2003) constructed a phylogenetic tree of prokaryotic 16S rRNA genes from studies on acid mine drainage and bioleaching sites. Lineages of α, β, γ, and δ-proteobacteria were all represented. The archaeal lineages of *Thermoplasmatales* were also shown. Both obligate autotrophic and facultative iron-oxidizing archaea have been found associated with AMD. More evidence for synergistic behavior between autotrophs and heterotrophs in AMD is apparent. A few eukarya were reported by Baker and Banfield (2003) which complement those described in Robbins et al. (2000) for Iron Mountain, California.

Recent studies have now shown that the often-studied and well-characterized *Acidithiobacillus ferrooxidans* is psychrophilic to mesophilic and not found at higher temperatures close to large masses of oxidizing pyrite or geothermal waters where the temperatures can be 25–70 °C. At these higher temperatures and lower pH values less than 1.5, *Leptospirillum* is more common as are iron-oxidizing archaea. One important finding is that archaea and leptospirilli are more common at the source of oxidizing pyrite where more extreme conditions of pH and temperature are likely to exist than downgradient (Baker and Banfield, 2003; Huang et al., 2011; Tan et al., 2009). For moderate conditions of pH and temperature in mine tailings, the microbial communities can vary substantially from site to site from bacterial domination to comparable bacterial and archaeal populations (Kock and Schippers, 2008). One of the most detailed chemical and microbiological investigations of downstream variations during Fe(II) oxidation was reported by Gónzalez-Toril et al. (2011). A 1,200 m stream flowing from the La Zarza-Perrunal mine in the Iberian Pyrite Belt was sampled at three points. Initial pH was 3.1 with Fe(III)/Fe(T) = 0.11 and containing some sulfate-reducers but increased in iron-oxidizers with downstream distance. *Leptospirillum* spp., *A. ferrooxidans*, and *Thermoplasmata* were found at all downstream locations. Iron-reducers were also found throughout the river. Green algae, especially *Chlorella*, were present near the origin as "continuous, green macroscopic biofilms, subsequently replaced by sporadic *Zygnematales* filaments." The most downstream sample had a pH of 1.9 and contained Fe(III)/Fe(T) = 0.99.

How microbes are able to tolerate low pH waters with high metal concentrations has long intrigued microbiologists. The reviews by Golyshina and Timmis (2005) and Baker-Austin and Dopson (2007) describe how acidophiles share distinct characteristics of highly impermeable cell membranes, reversed membrane potentials that deflect inflow of protons, and rapid proton pumps that pump excess protons out of the cell.

Numerous investigations have been reported on microbial life in the Rio Tinto mining area of southwestern Spain (López-Archilla et al., 2001; Gónzalez-Toril et al., 2003). The dominant prokaryote in the river itself is *Leptospirillum* and several strains were identified (García-Moyano et al., 2008). Comparison of microbial communities between the sediment and the water column showed some similarities in strains but higher cell density and higher richness occurred in the sediment (García-Moyano et al., 2012). One study of an extremely acidic pyritic leachate (pH = 0.61–0.82, 134 g/L of sulfate) from San Telmo mine in the Iberian Pyrite Belt was found to be dominated by *Ferroplasma* spp. with minor amounts of leptospirilli and acidithiobacilli (Sánchez-España et al., 2008a).

4. Hydrogeological processes

4.1. Physical movement of water, gases, and dissolved substances at mine sites

The movement of water and gases in mine wastes is closely linked to the quantity and quality of AMD that is generated at a mine site, therefore an understanding of hydrogeological processes is essential for predicting the quantity and quality of discharge waters and temporal changes to the volumes and composition. Rates of water flow are controlled by the overall hydrogeological setting, but also the location and degree of exposure of geological materials which contribute to the generation of low-quality drainage. For example, sulfide-bearing minerals exposed through excavation in mine workings and open mines will have different degrees of rock/water interaction than minerals that have been finely crushed and deposited in a mine tailings impoundment. The particle size and morphology of sulfide grains and the degree to which the particles are encased in host rock determines the extent to which exposed surfaces are available for reaction. The contact time between water and sulfide minerals is dependent on the geometry of the waste pile and local hydrological processes.

4.2. General considerations for different physical settings

4.2.1. Underground workings

Underground workings consist of a series of open caverns, ventilation shafts, adits, etc., all excavated typically into relatively intact rock. These features can allow enhanced infiltration of meteoric water into underground workings, which may discharge after little contact with sulfide minerals, after long periods of time as pools within the mine workings, or as flow into surrounding geological materials. Fracturing of rock associated with blasting and partial collapse of the workings results in the development of rough and uneven wall-rock surface exposures and three-dimensional fracture networks, which result in extensive exposed surface areas. Estimates of scaling factors relating the magnitude of exposed surface areas to idealized two-dimensional surface areas estimated from mine plans range from <20 to >100 (Morin and Hutt, 1997). These extensive exposures of reactive surfaces result in enhanced sulfide oxidation and increased rates of solute release to mine waters. For example, the combination of large exposed surfaces and an abundant supply of O_2 has led to the generation of AMD with exceptionally elevated concentrations of dissolved constituents (e.g., Nordstrom and Alpers, 1999b; Nordstrom et al., 2000).

4.2.2. Open-pit operations

Open pits are excavated to gain access to near-surface ore bodies. Recent advances in mining techniques and extraction procedures have resulted in an increase in the development of low-grade, large-volume ore bodies, including Cu and Au ore deposits. Open pits are developed as a series of benches which are pushed back occasionally to allow deeper excavation while maintaining stability of the pit walls. Mine development frequently requires dewatering by pumping from the base of the pit or by extraction of groundwater from wells or dewatering galleries. These activities expose sulfide minerals and associated gangue minerals in the pit walls and rubble zones at the base of the open put to water and atmospheric O_2 (Castendyk et al., 2015a, 2015b). Because of irregularities in the pit walls and extensive fracturing, the surface area of sulfide minerals exposed through excavation may be far greater than the idealized pit shell. Open pits may operate for periods from a few years to many decades, providing the potential for extensive sulfide oxidation. During active operation, pit walls may be flushed occasionally by precipitation, resulting in release of dissolved constituents to the pit drainage water. During periods of long desiccation, efflorescent minerals may accumulate on pit walls and within fractures.

After mining ends, many open pits are allowed to flood, resulting in the development of pit lakes. The water balance for the pit lake includes incident precipitation, evaporation, and surface water and groundwater inflows and outflows. Water quality of pit lakes is affected by dissolution of oxidation products previously accumulated within the open pit, by reactions between the pit lake water and surrounding geological materials, and by the water quality of surface water and groundwater inflows. In many cases, open pits are connected to underground workings, which may further affect water quality. Because of these influences, pit lake water quality can be highly variable. For example, a comparison of water chemistry of 22 mine pit lakes within the Iberian Pyrite Belt in Spain by Sánchez-España et al. (2008b) showed the common development of thermal and chemical stratification with a well-defined chemocline. The chemocline separated the anoxic Fe(II)-rich monimolimnion from the well mixed, oxygenated upper layer. A detailed review of the hydrology and geochemistry of open pits is provided by Castendyk and Eary (2009) and Castendyk et al. (2015a,b).

4.2.3. Waste-rock piles

Waste rock is composed of the poorly mineralized rock that surrounds ore bodies, which is excavated to gain access to the ore deposit. Although the largest accumulations of waste rock are associated with open pit mining operations (Lefebvre et al., 2001; Ritchie, 2003; Amos et al., 2015) many underground mines produce substantial waste rock piles. The generation of low quality drainage in waste rock piles is controlled by strongly coupled interactions between gas transport, water flow, and solute transport, microbially mediated geochemical reactions and the mineralogy of the waste materials and secondary reaction products. External forcings, including those due to variations in wind velocity or ambient temperature, can drive changes in temperature, pore-gas concentration, and pore-gas pressures within the waste rock pile, influencing sulfide oxidation rates (Amos et al., 2009). Heat generation associated with bacterially mediated sulfide oxidation can result in the development of thermally driven convective gas-transport cells, which can drive oxygen transport deep into the waste rock pile, expanding the volume of rock undergoing active oxidation (i.e., Cathles, 1994; Lefebvre et al., 2001; Ritchie, 2003). A comprehensive description of waste rock hydrology, geochemistry and mineralogy, and the potential for AMD generation in waste rock is provided by Amos et al. (2015).

Waste rock piles contain a mixture of coarse rock and fine-grained materials, therefore a mixture of large void spaces intermingled with zones containing small pore spaces. As a result of this heterogeneity, the hydrological regime within the waste rock pile is complex. Due to capillary constraints, the majority of the pore water typically flows through interconnected zones of partly saturated fine-grained materials (Neuner et al., 2013). During periods of increased infiltration associated with intense precipitation events, pore-water pressures may be sufficient to displace water from the fine-grained matrix into larger voids, resulting in rapid macropore flow.

Gas transport in waste rock piles is also affected by the grain-size distribution of the rock. Modern mining techniques favor the construction of large-scale, end-dumped high-wall waste rock piles. This disposal technique enhances segregation of the rock, resulting in the development of a coarse-grained rubble zone at the base of the pile and a thinner and less continuous zone of fine material near the pile surface. This structure enhances gas transport into the pile. Because of the presence of the large void spaces, O_2 penetrates deeply into the waste rock at the base of the pile, promoting extensive sulfide oxidation reactions in this zone (Amos et al., 2015). The exothermic sulfide oxidation reactions generate heat, resulting in the development of thermally driven gas convection cells, which can expand the zone of active sulfide oxidation into the central portion of the pile and result in increased acidification and solute release.

As sulfide mineral oxidation progresses, reaction products are transported through the pile, interacting with other minerals contained in the wastes (Smith et al., 2013). These reactions can result in neutralization of acidic pore water or can result in the formation of secondary minerals and gases that accumulate along the flow paths. Subsequent dissolution of these precipitates can result in release of solutes which can then be transported through the waste rock piles to underlying aquifers or to surface water bodies.

4.2.4. Tailings piles and impoundments

Tailings consist of flotation-concentrator wastes. Tailings are finely ground and most commonly transported through pipelines and disposed of as wet slurries in impoundments or increasingly using paste and dry stack disposal approaches. After the initial deposition of tailings, drainage of the slurry waters often occurs allowing the upper tailings to become exposed to atmospheric O_2. Because of the fine-grained nature of the tailings, the water content in the pore spaces of tailings impoundments can remain fairly high, limiting advective transport of oxygen. In most impoundments O_2 ingress occurs through diffusion and may be restricted to the upper few metres of the tailings (Blowes and Jambor, 1990; Johnson et al., 2000; Moncur et al., 2005; Lindsay et al., 2015). Gunsinger et al. (2006a) conducted a study of gas transport in pyrrhotite-rich mill tailings at the Farley mine site, Lynn Lake, Ontario. At this site, mill tailings were segregated on the basis of grain size, with the fine-grained tailings deposited in a separate section of the tailings impoundments. As a consequence of this deposition strategy, the moisture content of the fine-grained tailings was greater than for the coarse fraction. Field measurements of pore gas O_2 concentrations and complementary mineralogical studies indicated more extensive sulfide oxidation in the coarse-grained tailings area with only limited oxidation of the fine-grained tailings. Numerical modeling incorporating field-based measurements of tailings particle size, sulfide content, and moisture content was conducted to estimate the intensity and duration of the sulfide oxidation process. A comparison of the simulation results indicated the potential for more extensive and prolonged sulfide oxidation in the portions of the impoundment containing coarse-grained tailings, resulting in greater release of SO_4^{2-}, Fe, and Ni.

Although gas transport in mill tailings is less rapid than is observed in waste rock piles, the sulfide content of tailings is generally greater, resulting in more extensive sulfide oxidation. In addition, the fine grained nature of the tailings limits the rate of infiltration of precipitation and can result in the transport of high concentrations of sulfide mineral oxidation products downward and laterally through the tailings. Reactions between these solutes and unoxidized tailings, or surrounding geological materials, can result in neutralization of the pore water pH and formation of secondary minerals.

As a consequence of the fine particle size, water flow through mill tailings is typically described using continuum flow models. Under these conditions, acid-neutralization and secondary mineral formation reactions tend to approach equilibrium or near-equilibrium conditions, resulting in the development of distinct acid-neutralization zones that are constrained by precipitation and dissolution reactions (Morin et al., 1988; Blowes and Jambor, 1990; Johnson et al., 2000; Gunsinger et al., 2006b). The common acid-neutralization sequence proceeds from dissolution of calcite and dolomite, followed by dissolution of siderite, Al hydroxide phases, and Fe(III) hydroxide phases. Johnson et al. (2000) defined acid neutralization zones within the Nickel Rim tailings impoundment, Sudbury, Ontario, and described constraints on metal mobility associated with transitions between predominant acid-neutralization mechanisms. For example, high concentrations of dissolved Ni were observed in regions where acid-neutralization predominantly occurred through dissolution of $Fe(OH)_3$ and $Al(OH)_3$, whereas much lower Ni concentrations were observed in zones characterized by equilibrium with respect to carbonate minerals. In addition to acid neutralization by primary and secondary carbonate and hydroxide phases, dissolution of aluminosilicate minerals also can contribute to acid neutralization (Moncur et al., 2005). Jurjovec et al. (2002, 2004) conducted an integrated study of acid neutralization mechanisms in mill tailings which combined laboratory column experiments and numerical modeling. The column experiment results indicated the development of a series of acid neutralization plateaus which were characterized by near equilibrium with respect to primary and secondary carbonate and hydroxide phases. The release of dissolved metals from the column was closely associated with the predominant acid neutralization mechanism, with Zn, Ni, and Co released during the initial stages of the acid-neutralization sequence, whereas sharp increases in the concentrations of Cd, Pb, Al, Cr, and V were observed as carbonate minerals were depleted and the pH declined to less than 4.5. A more comprehensive discussion of the geochemistry, hydrology, and microbiology of mill tailings is provided by Lindsay et al. (2015).

4.2.5. Coal mine drainage

Full analyses (all major solutes and important minor or trace constituents) of coal mine drainage are difficult to obtain and not commonly done. An important exception is the report by Cravotta (2008a) who compiled water chemistry data from 140 abandoned anthracite and bituminous coal mines in Pennsylvania. Values for pH ranged from 2.7 to 7.3 and SO_4 concentrations up to 2,000 mg/L. In a sequential paper, Cravotta (2008b) examined the controls on the water chemistry and concluded that they could be explained by dilution and neutralization of acid waters by carbonate-buffered groundwaters, solubility limits by precipitates of Al, Fe, Mn, Ba, and Sr, and SO_4 complexation and sorption reactions. More recently, Cravotta and Brady (2015), documented a wide range of concentrations of major and trace constituents in untreated and treated effluent from coal mining and processing facilities. Generally, with treatment to pH 6 or higher and the removal of Fe to <7 mg/L and Mn to <5 mg/L, most trace constituents were attenuated to concentrations meeting criteria for maximum concentrations for freshwater aquatic life. However, constituents that accounted for most of the salinity were relatively unaffected by traditional treatment to increase pH and remove metals.

Feng et al. (2014) reviewed water chemistry data from 269 mines in 11 major coal-mining districts in China. Values of pH ranged from 2.0 to 9.0 and SO_4 concentrations ranged from 5.0 to 4,654 mg/L. Occasionally F concentrations were high, up to 5.93 mg/L, Mn concentrations were high, up to 32 mg/L, and Cl concentrations were also found high in some areas, up to 9,500 mg/L often associated with seawater intrusion. Some waters were saline, up to 22,200 mg/L dissolved solids. Six general categories of drainage were identified: (1) slightly contaminated (and easily treatable for re-use), (2) acidic (typically found in southern China and correlates with higher pyrite content), (3) high salinity, (4) high SO_4, (5) high F, and (6) high Fe and Mn. They found that there was a general correlation of water chemistry with the hydrogeological characteristics of the region. Over 6.1 billion m^3 of coal mine drainage are estimated to discharge annually in China.

5. Models

5.1. Geochemical speciation models

Aqueous speciation models are an essential part of any geochemical modeling of water–rock interactions. With sufficient analytical and field data on water samples, a speciation computation can provide information on different species of the same element dissolved in water *except* for redox species. For example, dissolved Ca may exist as the free ion, Ca^{2+}, or as a $CaSO_4^{\circ}$ ion pair, or as a $CaHCO_3^{+}$ ion pair. Speciation of an element affects its solubility, toxicity, bioavailability and bioaccessability, and sorption. Unfortunately, reliable determination of redox species requires analysis, it cannot be computed except for Fe speciation at pH values below 4. Even then it is preferable to directly measure the redox species. With reasonably complete analysis (all major solutes and selected trace elements and redox species of concern), verified QA/QC (quality assurance/quality control), and field parameters (temperature, pH, specific conductance, any necessary field determinations such as dissolved oxygen or dissolved sulfide), a reasonable speciation can be computed. The conceptual, mathematical, and chemical framework for these computations can be found in several reviews and books (Brinkley, 1947; White et al., 1958; Smith and Missen, 1982; Nordstrom and Munoz, 1994; Nordstrom and Campbell, 2014).

As part of the QA/QC used to determine the reliability of a water analysis, a charge balance calculation should be performed. A charge balance takes the millequivalents of cations, subtracts the millequivalents of anions and divides by the average or the sum and expressed as a percentage. It should be noted that for waters with a pH below 3 and hydrogen ion a major cation, a chemical model is necessary to compute the charge balance (Nordstrom et al., 2009). Often the hydrogen ion is not used to compute the charge balance and this omission results in serious errors for acid waters. Recently, McCleskey et al. (2012) introduced a further constraint by incorporating a calculation of conductivity into the WATEQ4F code. Now it is possible to identify whether a cation or an anion is responsible for an error in the charge balance.

As an example of how speciation can lend insight into geochemical processes that occur in mine environments, Nordstrom (2011) demonstrated that the 1–3 orders of magnitude supersaturation commonly observed with respect to freshly precipitated ferric hydroxide is largely an artifact of nanocolloids (or iron–organic complexes) passing through filter membranes and being analyzed as dissolved iron(III) after sample acidification. This effect was shown by an examination of about 1,300 water samples influenced by acid drainage (both natural and mine drainage) for which Fe(II/III) determinations had been done and complete water analyses were available. After samples had been screened by appropriately applied detection limits and the Fe(II/III) determinations were checked against redox potential measurements, the supersaturation largely vanished.

Another example of a solubility control limiting concentrations is shown by the saturation indices for aluminum hydroxide relative to pH (Fig. 6; Nordstrom, 2011). At pH values below 4–4.5, Al behaves conservatively and tends to move with the water but once the pH has increased from below 4 to about 4 for groundwaters or about 4.5 for surface waters or higher, Al hydrolyzes and becomes quite insoluble (Nordstrom and Ball, 1986). The hydrolysis and precipitation of Al provides a good example of how sensitive the solubilities of metals are to their first hydrolysis constant. For Al the $pK_1 = 5.0$ (Nordstrom and May, 1996) which is the pH where Al^{3+} activity = $Al(OH)^{2+}$ activity ('activity' is used here in the thermodynamic sense of the molality times the activity coefficient; Nordstrom and Munoz, 1994). Hence, at pH values slightly less than 5 hydrolysis begins and hydrolysis is necessary for the precipitation of a hydrolytic phase such as microcrystalline gibbsite or basaluminite (Bigham and Nordstrom, 2000).

This generalization about Al geochemistry has been in the context of surface waters or underground running mine waters. For waters with more residence time, such as groundwaters, waste

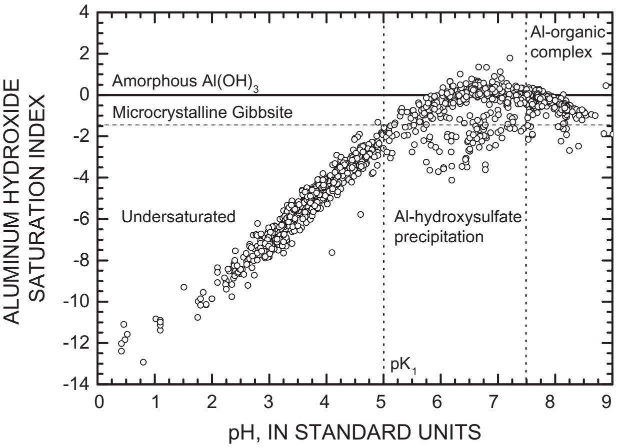

Fig. 6. Geochemistry of Al for 1383 mining-influenced surface water samples from the western U.S. The saturation index for amorphous $Al(OH)_3$ is plotted against pH with three zones demarcated by vertical dotted lines: at pH values below 5 waters are undersaturated with respect to gibbsite or amorphous $Al(OH)_3$, for pH values between 5 and 7.5 saturation is reached with respect to $Al(OH)_3$, and for pH values about 7.5 a decreasing trend in saturation indices is suggestive of organic–Al complexing (from Nordstrom, 2011).

rock pore waters, and tailings pore water, the attenuation of Al occurs at slightly lower pH values, closer to 4 than 5, and indicates a pH buffering reaction (Blowes et al., 2013). The attenuation of Al in subsurface waters near pH 4 is correlated with some silica attenuation in the ARD near Questa, New Mexico (Nordstrom, 2008) and may be related to the formation of an insoluble aluminum–silica oxyhydroxide phase (Hochella et al., 1999; Exley et al., 2002).

Numerous applications of geochemical speciation models have provided insight into the precipitation, sorption, and reactive transport processes of acid mine drainage. These models have been incorporated into computer codes which may differ in range and capability. Periodically these codes and their limitations are reviewed or compiled (e.g., Bethke, 2008; Zilberbrand, 2012; Birkle, 2012; Nordstrom and Campbell, 2014). A review of these codes is beyond the scope of this paper but sufficient information exists in these references.

5.2. Coupling of transport and geochemical reactions

Recent advances in understanding the generation of AMD requires information on the extent to which the physical flow system is coupled to the rate of sulfide mineral oxidation, acid neutralization processes, and other reactions which can control the mobility of constituents contained in AMD. Highly-constrained sampling programs which integrate measurements of water flow, gas flow, sulfide mineral oxidation rates, acid neutralization rates, microbial community analysis, and secondary mineral precipitation rates, provide data required to understand the mechanisms controlling the quality of the effluent as it discharges from a mine site and moves into the adjacent environment and to predict temporal changes in the effluent quality. Early applications of reactive solute transport models to describe the generation and transport of low-quality drainage at mine sites includes coupling of transport equations with equilibrium reactions in water-saturated aquifers (e.g. Cederberg et al., 1985; Walter et al., 1994), followed by numerical simulations of processes within tailings impoundments including reactions occurring in the unsaturated zone (e.g. Wunderly et al., 1996), followed by incorporation of reaction kinetics to more closely reflect observed processes (e.g. Mayer et al., 2002; Brookfield et al., 2006). These models provide close approximations for geochemical processes occurring in settings such as mine tailings impoundments and adjacent aquifers characterized by more uniform flow than observed in mine workings and waste-rock piles. In these studies, comprehensive data sets of physical and geochemical parameters were collected and used in conjunction with model development. The application of a reactive solute transport model to predict the long-term evolution of water quality in a more complex hydrogeological setting such as waste rock piles relies on a combination of high-quality data collected over many years of waste-rock pile evolution. Together, an integrated approach may provide insight into the complex interactions among spatially variable water flow, mineralogy, grain size distribution, and changes in climatic conditions.

6. Role of scientific research in remediation

Remediation of most mine sites is a challenging undertaking and requires considerable multidisciplinary skill and experience. Very few universities offer courses or a curriculum that cover the skill set in geology, chemistry, geochemistry, hydrology, microbiology, biology, and engineering (civil, mining, and environmental) that is needed to cover the topics useful to develop remedial options that are effective over the time frames over which low-quality drainage is generated at typical mine sites. Consequently, a multidisciplinary group is needed to plan and execute successful remediation and a multidisciplinary oversight committee is needed to provide independent advice and counsel. Guidance on remedial options has been available through several sources, e.g. UNEP (1994, 1997), the GARD Guide (GARD Guide, 2009), numerous MEND reports (MEND, 2002-present), the ADTI series of handbooks (McLemore, 2008; Gusek and Figueroa, 2009; Castendyk and Eary, 2009), Younger et al. (2002), and DeGraff (2007). In this section summary comments are shared regarding the importance of scientific research in obtaining more effective remediation.

Disconnects between scientific research, engineering capabilities, and economic feasibility have often hindered effective remedial efforts. Developments in research can have a direct bearing on evaluating remedial options, planning remedial design, and executing remediation. Also, problems encountered in engineering design or execution can often be resolved by focused research.

Results of scientific research have both explanatory and predictive power. Explanatory power is important because if one can explain how a particular system works then there is a much better chance of designing properly an effective remedial system and correcting problems with it. Predictive power is important because it offers the possibility of exploring the potential results of various alternative actions and avoiding unintended consequences. Characterization of a mine site or of mine wastes is supposed to provide the necessary information to identify the main sources of contamination and the main pathways to environmental receptors for risk assessment. If the site being characterized is in the environment with geologic, hydrologic, geochemical, mining and mineral processing, biological, and microbiological aspects, then appropriate experts in these areas need to be consulted.

Research was necessary to answer the question posed by USEPA Region 9 (western region): What happens if we plug the main mine portal at the Iron Mountain Mines Superfund Site? After collecting underground data on the occurrence of negative pH water (Nordstrom et al., 2000) and the growth of abundant efflorescent salt formation (10 m high columns of rhomboclase, coquimbite, and voltaite), the answer was that a 600,000 m^3 mine pool of pH <1 water with grams per liter of dissolved metals would form above the water table in a crystalline rock with little neutralizing capacity. Furthermore, it would leak out at numerous undisclosed locations where it would be difficult to capture. This was one of several reasons why it was considered unacceptable to plug the mine. Other mines have been plugged, often with deleterious results similar to the unacceptable Iron Mountain scenario. These consequences were possible to predict because of research carried out at Iron Mountain and supplemental characterization of the site after underground excavations were made accessible combined with years of interpretive techniques for water chemistry (Alpers et al., 2003; Nordstrom et al., 2000; Glynn and Plummer, 2005; Plummer et al., 1990; Parkhurst and Appelo, 2013; Pitzer et al., 1977).

Another outgrowth of research was the development of tracer-injection with synoptic sampling for quantifying solute loads from mine sites and for providing basic data needed for reactive-transport modeling of streams and rivers affected by mine drainage. Several studies and advances in this important technique were summarized by Nordstrom (2011). Runkel et al. (2012) performed a post-audit study on Mineral Creek, Colorado in which the OTEQ reactive-transport code was calibrated on existing low-flow conditions. Then Runkel et al. predicted conditions during treatment without knowledge of those conditions. Conditions during treatment were measured and compared to predictions and found to be comparable for Al, Fe, pH, and Pb concentrations, but not so comparable for Cd, Cu, Zn, and As. The main problem for inaccurate comparisons seemed to be caused by difficulty in specifying the amount of precipitated Fe available to sorb metals. A more detailed investigation of replicate sampling campaigns for Peru Creek, Colorado, examined sources of error from analytics, field sampling, and temporal variations during the application of synoptic mass balances. The study successfully identified main sources of uncertainty (Runkel et al., 2013).

Numerous field techniques, laboratory techniques, and model and code development grew out of considerable research on groundwater geochemistry, mine waste geochemistry, and reactive-transport studies, and cooperative interaction between researchers and regulatory agencies and industry. The challenge of complex mine site remediation is best met with continued cooperation between research and remediation.

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