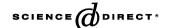


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Review article

Acid Mine Drainage (AMD): causes, treatment and case studies

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Abstract

This paper describes Acid Mine Drainage (AMD) generation and its associated technical issues. As AMD is recognized as one of the more serious environmental problems in the mining industry, its causes, prediction and treatment have become the focus of a number of research initiatives commissioned by governments, the mining industry, universities and research establishments, with additional inputs from the general public and environmental groups. In industry, contamination from AMD is associated with construction, civil engineering mining and quarrying activities. Its environmental impact, however, can be minimized at three basic levels: through primary prevention of the acid-generating process; secondary control, which involves deployment of acid drainage migration prevention measures; and tertiary control, or the collection and treatment of effluent.

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1. Introduction

The mining of certain minerals, including gold, copper, and nickel, is associated with acid drainage problems that can cause long-term impairment to waterways and biodiversity. Furthermore, some effluents generated by the metals mining industry contain large quantities of toxic substances, such as cyanides and heavy metals, which have serious human health and ecological implications [1].

Acid Mine Drainage (AMD) is produced when sulfide-bearing material is exposed to oxygen and water. The production of AMD usually — but not exclusively — occurs in iron sulfide-aggregated rocks. Although this process occurs naturally, mining can promote AMD generation simply through increasing the quantity of

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sulfides exposed. Naturally-occurring bacteria can accelerate AMD production by assisting in the breakdown of sulfide minerals.

Also referred to as acid rock drainage (ARD), AMD emanating from mine waste rock, tailings, and mine structures, such as pits and underground workings, is primarily a function of the mineralogy of local rock material and the availability of water and oxygen. Because mineralogy and other factors affecting AMD formation are highly variable from site-to-site, predicting the potential for AMD can be exceedingly challenging and costly [2]. Characterized by low pH and high concentrations of heavy metals and other toxic elements, AMD can severely contaminate surface and groundwater, as well as soils [3].

Every mine is unique in terms of its AMD potential; thus, the nature and size of the associated risk and feasibility of mitigation options will vary from site-tosite. There are no standardized methods for ranking, measuring and reducing the risk of AMD. Considering how large the penalties can be for miscalculating any of

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the aforementioned variables, the onus is on the individual mining companies to take charge of their own destinies on this front. It must begin with recognition that there are AMD hazards at individual sites, and that they give rise to specific risks. Where AMD is inevitable or likely, it makes sense to gear the response to the probability of serious consequences, which requires site-specific research to be undertaken. In mining regions where AMD has not yet formed, research should be carried out to identify ways in which it can be prevented. Mine planners and managers must therefore be equipped with the knowledge and tools to control AMD — specifically, to identify techniques that will minimize AMD impacts on life forms and their support systems [4].

There are many types of sulfide minerals. Iron sulfides are most common but other metal sulfide minerals may also produce AMD. Upon exposure to oxidizing conditions, the sulfide minerals oxidize in the presence of water and oxygen to form acidic, sulfate-rich drainage. Metal contamination associated with AMD depends on the type and amount of sulfide mineral oxidized, as well as the type of gangue minerals present in the rock. The oxidation of sulfide minerals and its subsequent acidity occurs through several reactions. The primary ingredients for acid generation are as follows: (1) sulfide minerals; (2) water or a humid atmosphere; and (3) an oxidant, particularly oxygen from the atmosphere or from chemical sources. In the majority of cases, bacteria play a major role in accelerating the rate of acid generation; the inhibition of bacterial activity can therefore impede the rate of acid generation.

This paper consists of a brief review of AMD at mine sites, followed by a summary of treatment methods. The paper also provides case studies of AMD treatment in old South African mines.

2. Occurrence of AMD

Releases of AMD have low pH, high specific conductivity, high concentrations of iron, aluminum, and manganese, and low concentrations of toxic heavy metals. Because most treatment technologies are either inadequate or too expensive, quite commonly, significant AMD is left untreated [5]. The reactions of acid generation are best illustrated by examining the oxidation of pyrite (FeS₂), which is one of the most common sulfide minerals. The first important reaction is the oxidation of the sulfide mineral into dissolved iron, sulfate and hydrogen:

$$FeS_2 + 7/2 O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (1)

The dissolved Fe²⁺, SO₄²⁻ and H⁺ represent an increase in the total dissolved solids and acidity of the

water and, unless neutralized, induce a decrease in pH. If the surrounding environment is sufficiently oxidizing (dependent on O_2 concentration, pH and bacterial activity), much of the ferrous iron will oxidize to ferric iron, according to the following reaction:

$$Fe^{2+} + 1/4 O_2 + H^+ \rightarrow Fe^{3+} + 1/2 H_2O$$
 (2)

At pH values between 2.3 and 3.5, ferric iron precipitates as Fe(OH)₃ and jarosite, leaving little Fe³⁺ in solution while simultaneously lowering pH:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3 \text{ solid}} + 3H^+$$
 (3)

Any Fe³⁺ from Eq. (2) that does not precipitate from solution through Eq. (3) may be used to oxidize additional pyrite, according to the following:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 (4)

Based on these simplified basic reactions, acid generation that produces iron which eventually precipitates as $Fe(OH)_3$ may be represented by a combination of Eqs. (1)–(3):

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$
 (5)

On the other hand, the overall equation for stable ferric iron that is used to oxidize additional pyrite (combinations of Eqs. (1)–(3)) is:

$$FeS_2 + 15/8O_2 + 13/2Fe^{3+} + 17/4H_2O \rightarrow 15/2Fe^{2+} + 2SO_4^{2+} + 17/2H^+$$
(6)

All of the above equations, with the exception of Eqs. (2) and (3), assume that the oxidized mineral is pyrite and the oxidant is oxygen. However, other sulfide minerals such as pyrrhotite (FeS) and chalcocite (Cu₂S) have other ratios of metal sulfide and metals other than iron. Additional oxidants and sulfide minerals have different reaction pathways, stoichiometries and rates, but research on these variations is limited.

In many environmental settings, the consequence of AMD is considered moderate to severe, mostly independent of pH and acidity. In other words, the environmental consequence is often considered at least moderate whether pH is 2 or 4 and whether acidity is 100,000 or 1000 mg/L [6].

The primary factors that determine the rate of acid generation are:

- pH;
- Temperature;
- Oxygen content of the gas phase, if saturation is less than 100%:
- Oxygen concentration in the water phase;
- Degree of saturation with water;
- Chemical activity of Fe³⁺;
- Surface area of exposed metal sulfide;
- Chemical activation energy required to initiate acid generation; and
- Bacterial activity.

Chemical, biological and physical factors are important for determining the rate of acid generation; physical factors, particularly waste rock dump permeability, are particularly important. Dumps with high permeability have high oxygen ingress, which contributes to higher chemical reaction rates, hence, higher temperatures and increased oxygen ingress through convection. Most testing of Acidithiobacillus ferrooxidans has involved oxidation of pyrite (FeS₂); however, the bacterium may accelerate oxidation of sulfides of antimony, gallium, molybdenum, arsenic, copper, cadmium, cobalt, nickel, lead and zinc. For bacteria to thrive, environmental conditions must be favourable. For example, A. ferrooxidans is most active in water with a pH of less than 3.2. If conditions are not favourable, the bacterial influence on acid generation will be minimal. This apparent importance of environmental conditions explains the contradiction in reported experimentation that shows bacterial influence ranges from major to negligible. In situations where bacterial acceleration is significant, there are additional factors that determine the degree of bacterial activity and the associated rate of acid generation.

Following the oxidation of a sulfide mineral, resulting acid products may either be immediately flushed by water moving over the rock or, if there is no water movement, can accumulate in rock, where it is later flushed. If the acid products are flushed from the sulfide mineral, they may eventually encounter an acid-consuming mineral; the resulting neutralization will remove a portion of the acidity and iron from solution and will neutralize the pH. Sulfate concentrations are usually not affected by neutralization — an indication of the extent of acid generation, even following neutralization by acid-consuming minerals.

3. Sources of AMD and selected case study analysis

AMD associated with underground mining has long been considered a serious environmental hazard. In such

settings, AMD often occurs as low pH water and can therefore be easily identified. More recently, AMD emanating from open pit workings has become a concern. Little is known of the potential danger posed by these operations, as most are still being worked or maintained. In this method of mining, large volumes of rock are initially subjected to an oxidizing environment. The danger of long-term lope deterioration continually making new rock surfaces available for oxidization suggests that substantial quantities of AMD could occur following closure. There are two sources of AMD, which are presented in Table 1.

Waste rocks, which contain sulfides, are a significant source of AMD; this makes the management of waste dumps of utmost importance. Within the broader definition of waste dumps lie spoil piles, tailings dams and spent heap-leach piles. Spoil piles have the potential to be extremely acidic, but accurate prediction of the pH of spoil run-off is difficult due to the self-neutralizing character of carbonate-containing spoils. Acidic overburden exacerbates acidic seep problems as no neutralization of effluent occurs once it has left the ore body. In coal seams containing calcite or in the absence of acidproducing materials, effluent is neutralized in situ, giving rise to circum-neutral or alkaline drainage. Alkaline drainage is not as environmentally damaging as AMD. Some alkaline waters have high concentrations of ferrous iron, which dramatically lowers the pH upon oxidation and hydrolysis, rendering the effluent acidic. Alkaline drainage is more common in underground mines than in surface mines.

South Africa is blessed with the occurrence of many minerals, often in large quantities and of strategic importance to it and to other nations. The country has one of the most sophisticated and developed mining industries in the world. The overall goal of managing environmental impacts in South Africa is to design and implement mitigating measures that minimize the residual impact of mining.

Fig. 1 is an old abandoned metalliferrous mine in the Republic of South Africa [7]. Here, mining ceased in early 1980s but a considerable amount of acidic-water continues to be released from abandoned underground

Sources of Acid Mine Drainage

Primary sources	Secondary sources
 □ Mine rock dumps □ Tailings impoundment □ Underground and open pit mine workings □ Pumped/nature discharged underground water □ Diffuse seeps from replaced overburden in rehabilitated areas □ Construction rock used in roads, dams, etc. 	 □ Treatment sludge pounds □ Rock cuts □ Concentrated load-out □ Stockpiles □ Concentrate spills along roads □ Emergency ponds



Fig. 1. Example from an old metalliferrous mine, South Africa.

workings into the surface environment. In this case, pyrite content is the main cause of water pollution. When exposed to air, pyrite oxidizes and forms sulphuric acid once coming into contact with water. The acid produced dissolves salts and mobilizes heavy metals from mine workings. Dark, reddish-brown water and pH values as low as 2.5 persist at the site.

In the abandoned colliery mine shown in Fig. 2, also in the Republic of South Africa [7], surface sinkholes resulting from the collapse of old workings have affected groundwater and surface water quality. Certain coal seams in this region are associated with pyrite, where water seeps to the surface and enters a local stream. This water has a high total dissolved solids (TDS) concentration and a low pH value. In an attempt to prevent underground water from entering the surface water environment and ecosystem, a series of dams were constructed.

All mines eventually close but if water is not controlled, it could acidify and re-enter the ecological system. In order to minimize the environmental impact of flooding water from old mines, a water treatment or

Fig. 2. Example from an old colliery, South Africa.

desalination plant can be constructed at the discharge point of the mine (Fig. 3), which enables mine water to be treated to a potable, industrial or agricultural standard (Fig. 4).

Currently, AMD is treated by adding lime to neutralize the acid and precipitate heavy metals as hydroxides. These can be flocculated, forming a high density sludge (HDS), which once settled can give a relatively clear overflow, and then discharged into rivers (the HDS process).

Some of the mines in South Africa on their own account have established treatment plants to treat AMD more satisfactorily (e.g. the GYP-CIX process at the Western Areas Gold Mine). Apart from current treatment methods, two exciting developments are highlighted which indicate that this may be turned into a remarkable opportunity. The first relates to the GYP-CIX process, which uses the well-known cation and anion exchange resins to absorb from the AMD, cations (e.g. Ca^{2+}) and anions (SO_4^{2-}) by exchanging them for hydrogen and hydroxide ions, respectively. This is a well-known method used to de-ionise solutions. When the resins are fully loaded with the pollutants, they have to be regenerated with an acid and an alkali, respectively. Conventionally, sulphuric acid and lime are used because of their low cost, which nevertheless represented 85% of the total operating costs of the GYP-CIX process. Some of the researchers suggest that nitric or phosphoric acid be used for the cation resin regeneration and ammonia or potassium carbonate or hydroxide for the anion resin. Although the cost of these reagents is much higher than the conventional ones, the regenerate effluents can be reacted with each other to form the well-known fertilizers ammonium and potassium nitrates and phosphates. After removing the precipitated calcium sulfate, a range of concentrated fertilizer solutions are obtained with the same intrinsic value as the industrial products, which are invariably



Fig. 3. Example of mine wastewater treatment plant, South Africa.

made by direct reaction between these same acids and alkalis.

In effect, the regeneration of the resins is achieved at close to zero cost, with no significant changes to the basic engineering features of the proven process. The total operating costs reduce to <R1.0 per m³. The modified process, known as the FERRIX Press, offers other advantages such as reduced capital costs. The product water is ideally suited for agricultural use.

The second development of immense significance was the establishment of an agricultural activity at Western Areas Gold Mine using partially-treated AMD to which fertilizers had been added to grow high-value fruit and olive crops using sophisticated control technology featuring drip irrigation. This activity is still operating successfully on waste land surrounding the mine. Phenomenal value outputs are achieved in the order of >R100,000 per ha, equivalent to an added value potential to the water used of >R20 per m³.

4. Control of AMD migration

Water is the basic transport medium for contaminants and consequently, all measures aimed at AMD migration control are concerned with the control of water flow. Control of water exit is of little value as long-term storage is negligible. Water entry into the site of acid formation may be controlled by:

- 1. Diversion of surface water flowing towards the site of pollution;
- 2. Prevention of groundwater infiltration into the pollution site;
- 3. Prevention of hydrological water seepage into the affected areas; and
- 4. Controlled placement of acid-generating waste.



Fig. 4. Tailings dam rehabilitation and vegetation.

Diversion most commonly consists of ditches, which are difficult to maintain for long periods of time, despite their easy initial construction. If possible, groundwater discharge areas should be avoided as isolation and interception of contaminated groundwater is very difficult to achieve. Under-drains can be installed in locations of dumps, and the infiltration by hydrological water can be further retarded through the use of sealing layers.

For open pit mines, several methods exist for the treatment of AMD. These include flushing, containment and evaporation, discharge (through wetlands), neutralization and precipitation, and desalination. Flushing is the process whereby water is drained rapidly from spoil heaps before they are able to accumulate to high levels. Ferrous iron may be removed before it is oxidized, thus preventing reaction with pyrite and the precipitation of ferric hydroxide. A major disadvantage inherent with this approach is generation of acidity outside the spoil by oxidation and precipitation of the dissolved iron. Containment involves flooding as much area of the spoils as possible, thereby preventing oxidation. Spoil water is then contained and prevented from being released into the environment. The method, however, has not been successful due to the difficulties associated with water level management in pits. Where AMD cannot be prevented or discharged, neutralization methods can be employed.

Treatment of mine effluent requires the establishment of a collection system capable of intercepting both surface run-off and groundwater flows. The former is readily achieved through the use of ditches but subsurface flow may require the installation of cut-off walls, trenches or wells.

5. Wetland process which can affect AMD

Wetlands at first site appear to be relatively homogenous environments, dominated by reeds. They are, in fact, complex ecosystems, representing a site of interaction between terrestrial and aquatic systems [7–10]. Wetlands typically comprise a mosaic of habitats, representing a range from permanently wet open water areas to temporary wet areas on the margins of wetland. Not only does the degree of wetness change, but soil properties may also change. The following properties may change: density, porosity, chemical composition, depth and the amount of organic matter. Soil properties may change as a function of both lengths along the wetland and width. The chemical characteristics, in particular the pH and redox potential, may change in response to water level change.

Some natural wetlands can remove iron, manganese and other metals from AMD. Limonite, or bog iron, was mined as the source of the USA's first ironworks, and is still a significant source of iron ore in northern Europe. Similarly, mixed oxides of manganese called wad or bog manganese are the product of less acidic wetland removal process. A number of physical and biological processes may contribute to changes in the water chemistry of mine drainage as it follows through a wetland. As wetlands are most often located at low spots in the landscape they can often intercept surface flows of uncontaminated water. If these flows are significant, they can cause changes in the water chemistry that could be mistakenly attributed to biological or chemical processes. Some researchers are currently in the process of developing a model incorporating both chemical equilibrium and kinetics into a wetland simulation model. This will permit at least an initial approximation of the likely fate of contamination entering and leaving a wetland.

Before actually dealing with mine drainage, it is useful to model the fate of iron and manganese in solution to establish whether it is chemically feasible to form insoluble precipitates and the condition necessary for their formation.

Dilution improvements in water quality may result from the accumulation of metals in plants and substrate, microbially mediated reduction processes, and abiotic or microbially-catalyzed metal oxidation and hydrolysis reactions because wetlands have heterogeneous environmental conditions. Owing to the variable composition of mine drainage and the dynamic and complexity of wetlands, it is virtually possible to predict the likely effluent from a wetland without resorting to modelling approach.

6. Neutralization processes

The most environmentally effective techniques available for mitigating AMD are internal neutralization methods, water-covers and biological/natural degradation processes [11]. A number of factors dictate the level of sophistication of the treatment system that is necessary to ensure that effluent standards will be met. These include: the chemical characteristics of the AMD; the quantity of water in need of treatment; local climate; terrain; sludge characteristics; and the projected life of the plant. The chemicals usually used for AMD treatment include limestone, hydrated lime, soda ash, caustic soda, ammonia, calcium peroxide, kiln dust, and fly ash. The following discussion highlights some of the characteristics of each of these neutralizing agents [12].

Lime neutralization/precipitation, referred to in mining circles as the "chemical process", is often used to treat AMD in the mining industry [13,14]. During lime treatment, the most commonly used process, AMD is discharged directly into a rapid mix chamber where hydrated lime is added in dry form or as slurry. Low

ferrous iron concentrations (<50 mg/L) are treated to a pH of 6.5–8.0 and then diverted directly to a settling chamber. Higher concentrations have pH 8–10 and are passed through an aeration tank, where the ferrous hydroxide precipitate is converted to ferric hydroxide. The water then flows to a settling chamber, where heavy metals are precipitated from the solution. Although limestone is generally an inexpensive reagent, and that its application produces a lower volume of sludge, it is not widely used, largely because carbon dioxide buffers the reaction, therefore making it difficult to raise the pH above 6. Limestone is also inefficient with high ferrous iron water, and the method of application is more complex than that involving lime.

The simplest method of neutralization involves the lining of a streambed with limestone, whereby water is treated as it flows over the limestone. However, this strategy is not necessarily effective because the limestone rapidly becomes coated with iron, calcium sulfate and biological growth, which inhibits interaction with mine water. Crushed limestone can also be added to the water. The split treatment of AMD with lime and limestone may yield the most desirable results.

7. Concluding remarks

The conventional method for treating AMD is the addition of a source of alkalinity to raise the pH above the threshold required by iron oxidizing bacteria, thereby radically reducing the rate of acid generation. The following benefits arise from this course of action:

- Removal of acidity and addition of alkalinity,
- Increase in pH,
- Removal of heavy metals,
- Ferrous iron oxidized more rapidly to ferric iron at lower pH,
- Sulfate can be removed once the solubility of calcium sulfate is exceeded by the addition of sufficient calcium.

Pyrite is the main cause of water pollution originating from abandoned mine workings and residue deposits. Management of AMD aims to reduce the impact of the effluent to levels that can be tolerated by the environment without significant damage. In order to minimize this pollution, precautions must be taken to ensure that rainwater does not come into contact with pyrite. Groundwater neutralized with lime or passive treatment systems, which rely on natural geochemical and biological processes for acid neutralization and precipitation—adsorption of metals, is widely used to prevent AMD. These systems include natural or man-made reed beds that are relatively inexpensive to construct for reasonable volume of water. With the necessary AMD

treatment measures in place, mine water can be treated to a potable, industrial or agricultural standard.

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