ACID MINE DRAINAGE

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When metal sulfide minerals are exposed to air and water, they break down and give rise to acidic, sulfate-rich waters contaminated with dissolved metals, particularly iron. Most commonly, this exposure is due to mining, and the waters are called acid mine drainage (AMD). Sulfides may also be exposed by natural processes or construction projects, and then the resulting contaminated waters are called acid rock drainage. In the USA alone, over 15,000 kilometers of rivers are polluted by AMD, a legacy of the mining of metals and coal. AMD reduces water quality, kills aquatic organisms, and makes receiving waters unsuitable for domestic and industrial use. By far the most important sulfide mineral contributing to AMD is pyrite (FeS_2). In this article we discuss the processes involved in AMD generation and in the management of AMD, focusing on pyrite as the source of contamination, and we demonstrate the role of "mineralogy" in our understanding of this problem.

PYRITE AND AMD GENERATION

Three steps characterize the AMD process (Fig. 1). The first step is the oxidation of the disulfide anion in pyrite to sulfate. This is an electrochemical reaction in which electrons are transferred from the pyrite surface to either O_2 or Fe^{3+}. These electrons come from sulfur atoms elsewhere on the pyrite surface. As the sulfur atoms become more electropositive, they react with adsorbed water molecules to form S–O bonds. When a sulfur atom has formed enough S–O bonds, it is released into solution. To maintain charge balance in the mineral, nearby iron atoms are released as Fe^{2+}. This process, which is quite complex as it involves the step-by-step transfer of seven electrons, produces a 1:1 ratio ferrous sulfate : sulfuric acid solution (Rimstidt and Vaughan 2003). The Fe^{2+} can remain in solution or, under evaporative conditions, it can be incorporated into one of many efflorescent ferrous sulfate minerals, such as melanterite ($FeSO_4 \cdot 7H_2O$) and rozenite ($FeSO_4 \cdot 4H_2O$), where it is retained until the minerals dissolve during a rain event. In the second step, Fe^{2+} is oxidized to Fe^{3+} by *Acidithiobacillus* spp. and related microbes (Baker and Banfield 2003). Fe^{3+} is a more effective oxidant than O_2 and it quickly reacts with more pyrite to increase the rate of acid production and Fe^{2+} release.
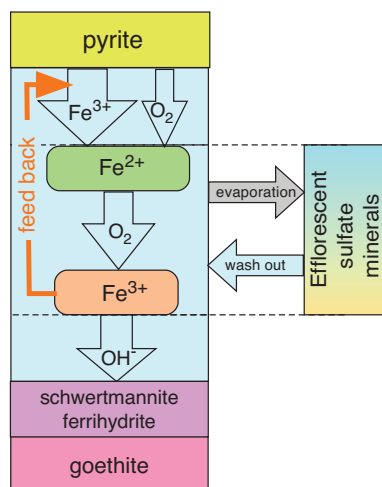
This creates a runaway condition where the iron released by pyrite oxidation causes even more pyrite oxidation; this lowers the pH to between 3 and 4, where iron-oxidizing microbes are especially active. The pH seldom drops below 2.5 because of the sulfate/bisulfate buffer. During dry periods some of the Fe^{3+} is stored in efflorescent sulfate minerals, such as copiapite [$Fe_5(SO_4)_6(OH)_2 \cdot 20H_2O$] and fibroferrite [$FeSO_4(OH) \cdot 5H_2O$], until rain events put it back into play. In the third step, consumption of hydrogen ions by reactions with bicarbonate ions (alkalinity) in receiving waters or by reaction with carbonate and silicate minerals causes the Fe^{3+} to hydrolyze and precipitate as ferric hydroxysulfate [schwertmannite, $Fe_8O_8(OH)_{8-2x}(SO_4)_x$] and oxy-hydroxide minerals [e.g. ferrihydrite, $Fe_{4-5}(OH,O)_{12}$], which eventually transform into goethite (FeOOH) or sometimes hematite (Fe_2O_3). Fe^{3+} hydrolysis releases more hydrogen ions and tends to offset the neutralization reactions.

It is important to note that the pyrite involved in AMD may contain a variety of minor contaminants, including As, Sb, and Cd (Abraitis et al. 2004); these are toxic to humans and other organisms at even low concentration levels and are released on pyrite breakdown. In AMD arising from the mining of metals, there are likely to be much higher concentrations of toxic elements coming from the oxidation of other sulfide minerals present. Minor and trace element contents, and stoichiometry, appear also to have a significant although still poorly defined effect on the rate of pyrite breakdown.

REACTION RATES

AMD develops when the acid production by pyrite oxidation and ferric iron precipitation exceeds the acid neutralization rate due to solution alkalinity and reaction with nearby minerals. Figure 2 compares the rates of some important AMD reactions as a function of pH. When pyrite is first exhumed and exposed to air, the surrounding solutions are at near neutral pH and the O_2 oxidation reaction is faster than the Fe^{3+} reaction. Fe^{2+} is converted to Fe^{3+} by abiotic oxidation about as fast as it is released from the pyrite. Pyrite oxidation and the subsequent Fe^{3+} hydrolysis both release hydrogen ions. If this rate is faster than the neutralization rate, the pH declines. Near pH 4 the solubility of Fe^{3+} increases to the point where it reacts with pyrite as fast as O_2, and as the pH drops below 4 the rate of oxidation of pyrite by Fe^{3+} increases very rapidly. At low pH the abiotic Fe^{2+} oxidation rate is slow and contributes very little Fe^{3+} toward pyrite oxidation. However, at low pH the rate of microbial Fe^{2+} oxidation is very fast and replenishes the Fe^{3+} as fast as it is consumed by reaction with pyrite. This creates a fast feedback loop that is responsible for runaway AMD production.
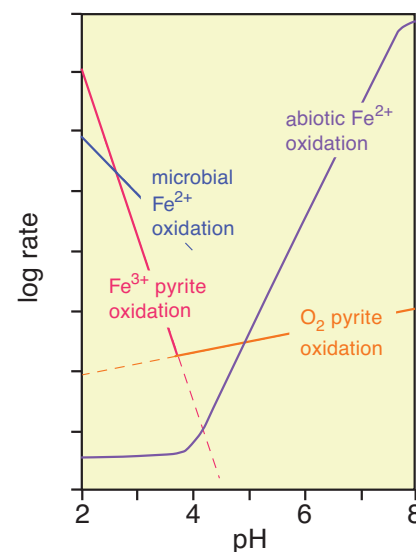

FIGURE 1 **The three steps of AMD**. In step 1, pyrite is oxidized by O_2 or Fe^{3+} and releases ferrous sulfate and sulfuric acid into solution. In step 2, Fe^{2+} is oxidized to Fe^{3+}. This reaction is catalyzed by acidophilic microbes. Much of the Fe^{3+} is consumed by fast reaction with pyrite. During dry periods some of the iron is stored in efflorescent sulfate salts but is returned to solution by rain events. In step 3, the Fe^{3+} undergoes hydrolysis to produce Fe^{3+} polymers, which aggregate into schwertmannite or ferrihydrite. These minerals eventually convert to goethite.

FIGURE 2 Relative rates of some important AMD reactions for air-saturated solutions with Fe^{3+} concentrations controlled by equilibrium with ferrihydrite (Williamson et al. 2006)

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SULFATE MINERALS

Most of the pyrite oxidation occurs in the unsaturated zone where the rate of delivery of O_2 by diffusion and advection is fast. Pyrite oxidation adds ferrous sulfate to the pore water, and during dry times some of this solution wicks to the surface, evaporates, and leaves behind efflorescent sulfate salts. Evaporation of a ferrous sulfate solution produces melanterite, but the mineralogy of these efflorescent salts evolves during dissolution–recrystallization cycles caused by diurnal humidity variation and by alternating rain events and dry periods. The salts undergo three kinds of chemical changes (Jerz and Rimstidt 2003). The first is simple dehydration; for example, melanterite with seven waters of hydration per formula unit converts to rozenite with four waters of hydration. The second change involves oxidation of Fe^{2+} to Fe^{3+}, yielding mixed-valence iron sulfate minerals such as copiapite. Eventually all the iron becomes Fe^{3+}, as in fibroferrite. The third change is neutralization, which causes some of the sulfate in the mineral formula to be replaced by hydroxide. Both copiapite and fibroferrite contain OH^- as well as SO_4^{2-} in their structures. In addition to these major chemical changes, efflorescent sulfate minerals incorporate a host of trace elements, sometimes in relatively high concentrations. For example, Cu^{2+} and Zn^{2+} often substitute for Fe^{2+} in their structures. Efflorescent salts, which form during dry times, are flushed into nearby receiving waters during rain events, causing dramatic pH declines along with very high trace element and sulfate concentrations (Nordstrom 2011). These washout events can cause fish kills.

HYDROXYSULFATE AND OXYHYDROXIDE MINERALS

Oxidation of Fe^{2+} to Fe^{3+} not only raises the activity of ferric iron but it consumes hydrogen ions and raises the pH. This reaction, along with any other process that raises the solution's OH^-/SO_4^{2-} ratio, encourages schwertmannite and ferrihydrite precipitation. These minerals form by a process involving ferric hydroxide polymers that grow to nanometer sizes and then aggregate (Banfield et al. 2000; Michel et al. 2007; Gilbert et al. 2013). These minerals are metastable and eventually convert to goethite (Schwertmann et al. 2004; Schwertmann and Carlson 2005) or occasionally hematite. Goethite can also precipitate directly from solution. Goethite often cements stream sediments, forming ferricrete. In upland settings the porous goethite plus hematite remnants of pyrite oxidation are called gossan.

AMD MANAGEMENT

AMD management schemes fall into two broad classes: those that treat the symptoms and those that treat the cause. All are costly and their effectiveness is usually site specific. A wide variety of treatments have been tried but there are few comparative studies of their relative effectiveness and economics, so choosing one for a site is an art guided by limited scientific understanding.

Once pyritic rocks have been exhumed and runaway AMD has commenced, limiting AMD production is expensive and complicated. It is cheaper and easier to raise the pH by mixing with neutralizing agents [NaOH, Na_2CO_3, $Ca(OH)_2$, $CaCO_3$] in stirred, aerated tanks. This pH increase causes rapid oxidation of Fe^{2+} and iron oxyhydroxide precipitation. The precipitating iron oxyhydroxides incorporate and remove most of the trace elements from the solution. Equipment costs and the pumping and stirring required for this treatment make it expensive. Smaller, less contaminated discharges are usually treated using less costly, passive treatment systems. These range from limestone-lined ditches and anoxic limestone drains to engineered wetlands. Fresh limestone neutralizes the acidity quite effectively, but precipitation of iron and aluminum oxyhydroxides, and occasionally gypsum, on the limestone grains reduces their reactivity over time (Huminicki and Rimstidt 2008). Fe^{2+} oxidation does not occur in anoxic limestone drains, so iron oxyhydroxide precipitation is avoided and treatment lifetimes are

extended. Engineered wetlands contain limestone and biochemically reactive organic matter that cause neutralization and convert sulfate to sulfide. Incorporation of trace elements into the precipitating sulfide minerals is an added benefit. Water retention ponds associated with these installations have the additional benefit of reducing storm washout effects on the receiving waters.

Ideally AMD management plans should treat the source to avoid or at least limit AMD production. Source treatment is usually too complicated and expensive for materials that have already been excavated and begun to generate AMD, so source treatment is usually applied during the excavation process. We know that AMD is caused by pyrite exposure to air and water, so limiting one or the other should decrease the problem. Restricting water access using soil covers or other hydrologic barriers to lower the pyrite oxidation rate will certainly curtail sulfate washout events. Covering AMD-generating material (Hammarstrom et al. 2005) at the I99 roadcuts near State College, Pennsylvania, with impermeable geofabric is an extreme example of this treatment. However, O_2 solubility and diffusion rate are very low in liquid water, so storing AMD-generating materials under water is a particularly effective way to limit pyrite contact with air. Various coatings on the pyrite surface offer another way to restrict O_2 access (Huminicki and Rimstidt 2009), but finding ways to specifically target pyrite has been difficult. Finally, because runaway AMD is due to the very fast microbial Fe^{2+} oxidation rates, a few schemes have been proposed to kill or incapacitate microbes using antibiotics or surfactants. Concerns about contamination of receiving waters by these treatments have limited their application.

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