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 due to mining, and the waters are called acid mine drainage (AMD). Acid sulfide minerals, such as copiapite [Fe₅(SO₄)₆(OH)₂·20H₂O] and fibroferrite [FeSO₄(OH)·H₂O], 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 Fe³⁺ to hydrolyze and precipitate as ferric hydroxysulfate [schwertmannite, Fe₈O₈(OH)₈·2x(SO₄)x] and oxy-hydroxide minerals [e.g. ferrihydrite, Fe₇.₅(OH)₁₂], which eventually transform into goethite (FeOOH) or sometimes hematite (Fe₂O₃). Fe²⁺ 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.

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 Fe²⁺ is stored in efflorescent sulfate minerals, such as copiapite [Fe₅(SO₄)₆(OH)₂·20H₂O] and fibroferrite [FeSO₄(OH)·H₂O], 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 Fe³⁺ to hydrolyze and precipitate as ferric hydroxysulfate [schwertmannite, Fe₈O₈(OH)₈·2x(SO₄)x] and oxy-hydroxide minerals [e.g. ferrihydrite, Fe₇.₅(OH)₁₂], which eventually transform into goethite (FeOOH) or sometimes hematite (Fe₂O₃). Fe²⁺ hydrolysis releases more hydrogen ions and tends to offset the neutralization reactions.

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**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 O₂ or Fe³⁺. 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 release Fe²⁺ as it is released from the pyrite. Pyrite oxidation and the subsequent Fe³⁺ hydrolysis both release hydrogen ions. If this rate is faster as it is consumed by reaction with pyrite. This creates a fast feedback loop that is responsible for runaway AMD production.
SULFATE MINERALS

Most of the pyrite oxidation occurs in the unsaturated zone where the rate of delivery of O₂ 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 Fe²⁺ to Fe³⁺, yielding mixed-valence iron sulfate minerals such as copiapite. Eventually all the iron becomes Fe³⁺, as in fibrophemrite. The third change is neutralization, which causes some of the sulfate in the mineral formula to be replaced by hydroxide. Both copiapite and fibrophemrite contain OH⁻ as well as SO₄²⁻ 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, Cu²⁺ and Zn²⁺ often substitute for Fe²⁺ 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 Fe²⁺ to Fe³⁺ 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⁻/SO₄²⁻ 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 ferricros. 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, Na₂CO₃, Ca(OH)₂, CaCO₃] in stirred, aerated tanks. This pH increase causes rapid oxidation of Fe²⁺ 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). Fe²⁺ 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 hydrologically barrier 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, O₂ 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 O₂ 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 Fe²⁺ 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.

REFERENCES


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