### THE MICROBIOLOGY OF ACID MINE DRAINAGE

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Acid mine drainage is a common problem in many parts of the country, originating from hardrock mines, strip mines or tailing piles. Most discussions on acid mine drainage refer to the physical process of oxidation while the role of microorganisms is left unnoticed. When iron containing minerals such as pyrite is first exposed during the mining operations, a slow chemical reaction with molecular oxygen occurs. While this abiotic reaction leads to the development of acidic conditions and the formation of iron precipitate, the degree to which acid mine drainage becomes an overwhelming burden on the environment results from the biologically catalyzed reactions of microorganisms.

# The Formation of Acid Mine Drainage

Iron exists in two oxidation states, ferrous (Fe<sup>2+</sup>) and ferric (Fe<sup>3+</sup>). Pyrite (FeS<sub>2</sub>), the most common form of iron and sulfur in coal and other ore bodies, is present in the reduced ferrous form. Although pH greatly influences the form in which iron is found, the electron potential for the Fe<sup>3+</sup>/Fe<sup>2+</sup> couple of +0.076 volts limits the ability to oxidize pyrite to only two electron acceptors, oxygen and ferric ions.<sup>1,9</sup>

When mine workings are first exposed to the atmosphere and water, the pH generally is neutral. Under these initial conditions, the ferrous iron in pyrite oxidizes spontaneously to ferric iron and highly insoluble precipitates of ferric hydroxide and ferric oxides. The stoichiometric reactions of pyrite are shown below:<sup>9</sup>

$$\begin{split} 4\text{FeS}_{2(s)} + 14\text{O}_2 + 4\text{H}_2\text{O} &\longleftrightarrow 4\text{Fe}^{2+} + 8\text{H}^+ + 8\text{SO}_4^{2-} \\ 4\text{Fe}^{2+} + 8\text{H}^+ + \text{O}_2 &\longleftrightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \\ 4\text{Fe}^{3+} + 12\text{H}_2\text{O} &\longleftrightarrow 4\text{Fe}(\text{OH})_{3(s)} + 12\text{H}^+ \end{split}$$



Figure 1. Acid Mine Drainage. (Photograph provided by Paul Hagerty.)

However, these stoichiometric equations do not provide the whole picture in acid mine drainage. As the initial reaction forms an acidic environment the ferrous ions become relatively stable. At pH values below 5.5, the rate of iron oxidation is extremely slow (k=10<sup>-25</sup> at 25°C). This, however, is contradictory to the phenomenon of acid mine drainage, in which pyrite is oxidized very rapidly to ferric iron at pH values of 2 to 3.

### Microorganisms in Acid Mine Drainage

Various microorganisms, such as *Thiobacillus ferrooxidans*, are able to catalyze the oxidation of ferrous iron to ferric iron.  $^{1,4,5,6,8,9}$  The ferric ions formed in the acidic conditions remain soluble and can readily react spontaneously with more pyrite, forming more ferrous ions, sulfate ions ( $SO_4^{2-}$ ) or precipitate.

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

The cycle continues as ferrous ions are again biologically oxidized to ferric ions (Figure 2). When acid mine drainage mixes with fresh water, the pH rises. Above a pH of 3, iron precipitates out of the water. The net result of these reactions is to produce  $4\text{Fe}(OH)_{3(s)}$ , (the reddish-brown water discoloration) and H<sup>+</sup> (a strong acid). In acid mine drainage environments where sulfuric acid is the dominant acid and large amounts of sulfate are present, ferric iron does not precipitate as the hydroxide, but as a complex sulfate mineral called jarosite (HFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>). This yellowish brownish precipitate has been termed "yellow boy" by early miners.

Thiobacillus ferrooxidans (Figure 3) is an acidophilic chemolithotroph that oxidizes ferrous iron as its primary energy-generating process. Since very little energy is generated in the oxidation of ferrous iron to ferric iron, these bacteria must oxidize large amounts of iron to grow. Even small numbers of organisms can be responsible for precipitating large amounts of iron.

Other microorganisms that may play a role thiooxidans, Ferrobacillus include Τ. ferrooxidans Leptospirillum and ferrooxidans.<sup>8,9</sup> Moderately acidophilic thiobacilli like T. neapolitanus, T. intermedios, and T. novellus have been found predominantly in ore samples with neutral pH values.<sup>8</sup> Studies have found that the reactions catalyzed by T. ferrooxidans in acidic environments provide the energy and nutrients to these various other microorganisms. (reference?)

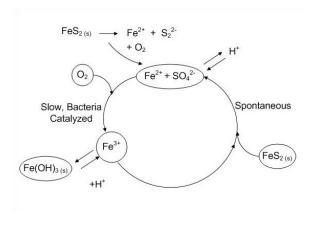


Figure 2. Mechanism of pyrite oxidation. (Adapted from Water Chemistry by Snoeyink and Jenkins. 1980.)



Figure 3. *T. ferrooxidans* cell suspension viewed by an electron microscope magnified 30,000 times. (Source: H.L. Ehrlich<sup>10,11</sup>)

#### **Treatment**

In order to develop remedial solutions to acid mine drainage, it is important to know the role these microorganisms play and their interaction with the chemical and physical reactions. Remediation techniques currently being used include constructed treatment wetlands or the application of a bactericide.

Passive treatment of acid mine drainage has been looked at as early as 1978. <sup>13</sup> Aerobic and anaerobic wetland systems, and settling ponds are typically combined with open limestone channels, diversion wells, anoxic limestone drains, or vertical flow reactors <sup>13</sup>, (padep, wvu) to treat acid mine drainage before it enters a



Figure 4. Constructed wetlands to treat acid mine drainage, Butler County, Pennsylvania. (Photograph by Jim Taylor.)

receiving body of water (Figure 4). These systems act to increase alkalinity, raise pH, precipitate iron and other dissolved metals, and promote sulfate reduction. Web sites maintained by the Pennsylvania Department of Environmental Protection and West Virginia University provide more detailed descriptions and design specifications for various treatment systems.

At sites with low pH environments where bacterial activity determines the rate of acid generation, inhibition of these bacteria can prevent acidification or greatly reduce the acidity that is produced. Surfactants, such as sodium lauryl sulfate or alkyl benzene sulfonate, have shown promise is providing cost effective bactericide at low pH (padep). Surfactant solutions can be applied to active tailing piles to prevent bacteria from reestablishing. However, surfactant treatment may not be appropriate for sites that have been reclaimed and the surfactant can not be applied directly to the pyritic material.

## **Beneficial Applications**

Although microbacteria are associated with the adverse effects from acid mine drainage, the same microorganisms are being used beneficially in the mining industry. The mining industry has successfully used biological separation technologies for a long time (references). Bioleaching uses microbacteria systems to remove minerals such as copper, gold, uranium and iron, and may be cost effective for low grade ores. Aerobic microbacteria bioleaching systems are possible for the removal of sulfide metals. In an aerobic system metals are leached through indirect and direct contact. Indirectly, microorganisms produce acidic conditions with the same mechanisms that cause acid mine drainage. The metals are removed from the ore as the solubility increases under acidic conditions. Organisms also directly act on some minerals that are susceptible to oxidation. New technologies using anaerobic bioleaching systems are being researched which operate under

neutral pH conditions and produces no acid bi-product.<sup>14</sup> Bacteria are also being researched that degrade cyanide for the use in conventional gold heap extraction.<sup>16</sup>

Borrowing from the mining industry, bioleaching is also being looked at for the recovery of metals from industrial waste and waste water.<sup>17</sup>

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