

Acid Mine Drainage: A Serious Environmental Problem of the Mining Areas

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Water discharge from mine drainage is usually acidic in nature, contains high concentration of heavy metal ions and mostly coloured. This discharge is referred to as Acid Mine Drainage (AMD) and continuously generated from active and abandoned mines, and overburden. AMD is considered the biggest environmental problem of mining industry and causes serious damage to aquatic and terrestrial ecosystems. Water resources are particularly affected by an AMD which has long-term, devastating impacts on rivers, streams and aquatic life in and around the mining area. The contamination of acid mine drainage into streams can severely degrade both habitat and water quality often producing an environment devoid of most aquatic life and unfit for desired uses. The severity and extent of damage depends upon a variety of factors including the quantity and quality of the AMD generated. Although, AMD can be generated from different types of mines, it is a serious problem in coal mines.

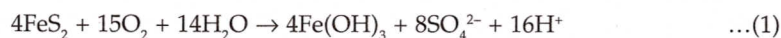
Formation of AMD

AMD results from the interactions of certain sulfide minerals with oxygen, water, and bacteria. The iron disulfide minerals pyrite (FeS_2) and, less commonly marcasite (FeS_2), are the principal sulfur-bearing minerals in bituminous coal. Pyrrhotite

(FeS), arsenopyrite (FeAsS), chalcopyrite (CuFeS₂) and other sulfide minerals containing Fe, Cu, As, Sb, Bi, Se and Mo also can produce acidic solutions upon oxidation. But these minerals are uncommon in coal beds. Pyrite is, therefore recognized as the major source of acidic drainage because of its wide distribution in coal and overburden rocks.

Pyrite (iron sulfide) in coal and overlying strata, when exposed to air and water, oxidizes, producing iron and sulfuric acid. Ferric iron, when discharged to surface water, hydrolyzes to produce hydrated iron oxide and more acidity. The acid lowers the pH of the water, making it corrosive and unable to support many forms of aquatic life. The level of acidity and the concentration of heavy metal pollutants in the mine drainage can be directly correlated to the amount of pyrite in the area around the mine.

Acid formation is most serious in areas of rainfall where rapid oxidation and solution of exposed minerals can occur. Physical weathering of the pyrite is an important step that reduces particle size of the mineral and exposes it to oxidation and hydrolysis. The overall stoichiometric reaction depicting the oxidation of pyrite is summarized below:



In this reaction solid pyrite, oxygen (O₂) and water (H₂O) are reactants, and solid ferric hydroxide (Fe(OH)₃), sulfate (SO₄²⁻), hydrogen ions (H⁺) and heat energy are products. The heat energy produced in this reaction for complete conversion of one mole of pyrite to ferric hydroxide amounts to about 1490 kilojoules at 25°C (Robie *et al.* 1978).

Chemistry of AMD formation

The investigations on geochemistry of AMD revealed that the reaction takes place in steps producing intermediates which are also the components of AMD and play important role in its chemistry (Stumm and Morgan, 1981). Presence of dissolved ferrous iron (Fe²⁺) in most samples of coal mine drainage indicates intermediate stage of the chemical reactions.

The first step in this geochemical process is the chemical oxidation of pyrite producing Fe²⁺, SO₄²⁻ and H⁺ ions as represented in the reaction 2.



The Fe²⁺ and H⁺ ions formed in reaction 2, are released into the waters and oxidized to form Fe³⁺ as shown in the reaction 3.

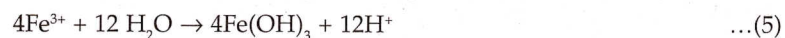


Reactions 2 and 3, which involve the oxidation of sulfur and iron, respectively, by gaseous or dissolved O₂, can be mediated by various species of sulfur and iron-oxidizing bacteria, notably those of the genus *Thiobacillus*. These bacteria require only dissolved CO₂, O₂, a reduced form of Fe or S and minor N and P for their metabolism and produce enzymes which catalyze the oxidation reactions. The energy released in oxidation reaction is used to transform inorganic carbon into cellular matter (Ehrlich, 1990). In well established acid-generating environments, the typical sequence is pyrite oxidation by reaction 2 to produce Fe²⁺, which is then oxidized to Fe³⁺ by bacteria via reaction 3. As a matter of fact, the Fe in AMD is found both as ferrous (Fe²⁺) from ferric (Fe³⁺) species in different concentrations depending on the pH of the medium. Because of the relative insolubility of Fe³⁺, most dissolved Fe in solutions with pH greater than about 3.5 occurs as Fe²⁺. At pH less than about 3 (the exact value depending on Fe and SO₄ content), major amounts of dissolved Fe³⁺ can be present.

The dissolved ferric iron (Fe³⁺) produced in reaction 3 is also the oxidizing agent for pyrite. It has been found that at acidic pH, rate of pyrite oxidation by Fe³⁺ is much faster than oxidation by O₂ (Williamson and Rimstidt, 1994). Thus, the Fe³⁺ produced in reaction 3 takes part in further pyrite oxidation as indicated in reaction 4. Although O₂ is not directly consumed in the pyrite-oxidizing step, it is necessary for the regeneration of Fe³⁺ to continue the pyrite-oxidation cycle.



As a final step, part or all of the Fe may precipitate as $\text{Fe}(\text{OH})_3$ as indicated in reaction 5. This process releases even more hydrogen ions into the aquatic environment and continues to reduce the pH. The iron hydroxide formed in this reaction is a yellowish-orange precipitate that turns the acidic runoff in the streams to an orange or red color and covers the stream bed with a slimy coating.



Hydrolysis and precipitation of iron solids, denoted as $\text{Fe}(\text{OH})_3$ in reactions 1 and .5, generally do not take place until the water is aerated and/or the acid is neutralized. The iron solids, which commonly form a reddish-yellow to yellowish-brown coating on rocks and other surfaces, can consist of a variety of amorphous or poorly crystalline ferric oxides, hydroxides or oxyhydroxysulfate minerals including ferrihydrite (variously given as $\text{Fe}_3(\text{OH})_4$, $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$, or $\text{Fe}_5\text{O}_3(\text{OH})_9$), goethite (FeOOH) and schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$) (Bigham *et al.* 1996). Ferrihydrite and schwertmannite are metastable and may ultimately dehydrate and recrystallize forming hematite (Fe_2O_3) or goethite. In acidic weathering environments, ferric sulfate compounds may form metastable intermediates prior to or in addition to ferric oxyhydroxide compounds (Nordstrom, 1982). Because the ferric sulfate minerals tend to be soluble and typically form under evaporating conditions, they can be significant sources of acidity and sulfate when later dissolved by runoff or recharge water at surface mines (Cravotta, 1994). Furthermore, other forms of sulfur, such as native S and $\text{S}_2\text{O}_3^{2-}$, can be intermediate products in the oxidation of pyrite (Moses *et al.* 1987), but these tend to oxidize to SO_4^{2-} under surface conditions. In addition to pyrite, sulfides of copper, zinc, cadmium, lead and arsenic will undergo similar geochemical reactions resulting in the contribution of toxic metal ions into mine waste water.

Factors Influencing Rate of AMD Formation

The kinetic of AMD formation greatly depends on many factors such as temperature, pH, pyrite chemistry and available

surface area for reaction, O_2 concentration and activity of iron-oxidizing bacteria. Hydrology and geology of the area also play significant roles in generation of AMD. These factors interact in a complex way and determine the influx of AMD.

Bacteria

Thiobacillus ferrooxidans is generally regarded as the principal iron-oxidizing bacterium involved in pyrite oxidation. The bacterium *Thiobacillus ferrooxidans* and several other species have the capability of catalyzing Fe^{2+} oxidation under acidic, aerobic conditions, and obtain the energy for their metabolism. Acidification progresses in a three-stage sequence dependent upon the activity of *T. ferrooxidans* and solution. During the first stage of this process, fine-grained pyrite can be directly oxidized by *T. ferrooxidans* or can be abiotically oxidized by air, with equal amounts of acidity produced by the oxidation of sulfide to sulfate and by the hydrolysis of Fe^{3+} . As the pH declines, abiotic oxidation of Fe^{3+} slows as much as 100-fold for each pH unit, and *T. ferrooxidans* takes on its primary role of oxidizing Fe^{2+} . This transition stage is referred to as stage two. Stage three begins when the decreased rate of $\text{Fe}(\text{OH})_3$ precipitation results in increased Fe^{3+} activity. The Fe^{3+} rapidly oxidizes the pyrite, producing Fe^{2+} that is then oxidized by the bacteria to Fe^{3+} . This cyclical reaction series greatly accelerates the rate of acid generation at many mine sites.

Because the rate of pyrite oxidation by Fe^{3+} is generally fast relative to the rate of oxidation by O_2 or the rate of inorganic Fe^{2+} to Fe^{3+} oxidation, the Fe^{2+} - Fe^{3+} oxidation is commonly rate-controlling and the bacteria are crucial in determining the rate of AMD formation. In addition to oxidation of dissolved Fe^{2+} , Thiobacilli also have the ability to oxidize pyrite directly, i.e., they can accomplish reaction 2 while directly attached to the pyrite surface (Chavarie *et al.* 1993). Although Fe^{3+} is formed rapidly at $\text{pH} > 4$, Fe^{3+} is relatively insoluble under these conditions and tends to form $\text{Fe}(\text{OH})_3$ or other solids, so that little Fe^{3+} remains in solution to oxidize pyrite. The net effect is that in the absence of bacteria, Fe^{3+} is either not produced at a

significant rate ($\text{pH} < 4$) or is so insoluble that its dissolved form is relatively unimportant as an oxidant of pH.

pH

The pH of the medium also plays important role in AMD generation. At pH value between 4 to 7 the rate of pyrite oxidation by O_2 is slow, and Fe^{3+} concentration is limited by the low solubility of $\text{Fe}(\text{OH})_3$. In increasingly acidic systems, Fe^{3+} is increasingly soluble. Since Fe^{3+} can rapidly oxidize pyrite, the oxidation of pyrite can be greatly accelerated at low pH. However, below about pH 1.5 to 2 the effectiveness of *Thiobacillus ferrooxidans* as a catalyst of Fe^{2+} oxidation decreases.

The generation of AMD can be understood by three sequential stages. Under stage one, when the pH is near-neutral or only slightly acidic, pyrite oxidation by reaction .2 proceeds by a combination of abiotic and bacterial mechanisms, and Fe^{2+} oxidation is primarily abiotic. Any biotic oxidation of pyrite is dominantly by bacteria attached to the surface of pyrite grains. In stage two, pH is generally in the range 3 to 4.5, and Fe^{2+} oxidation is mainly by *T. ferrooxidans*, because abiotic oxidation is so slow. In stage three, at pH less than about 3, the concentration of Fe^{3+} becomes high enough that escalates the rate of pyrite oxidation. This stage is responsible for production of the most acidic AMD. It should be noted that this sequence is based on processes in unsaturated systems with an adequate supply of O_2 and negligible alkaline material. In environments of limited O_2 and/or significant carbonate or other alkaline material, a different sequence of processes may occur.

Pyrite surface area

Kinetic studies indicate that the rate of acid generation depends on the surface area of pyrite exposed to solution, and on the physical and chemical properties of the pyrite surface. In general, rock with a high percentage of pyrite produces acidity faster than rock with a low percentage of pyrite. Also, a given mass of pyrite in small particles with high surface area will

tend to oxidize more rapidly than the same mass composed of coarse smooth-surfaced grains.

Oxygen

As oxidation of pyrite is the basic chemical reaction in AMD formation, availability of oxygen is most important variable in determining the rate of generation. Atmospheric O_2 is required for the direct oxidation of pyrite and for regeneration of Fe^{3+} . Thus, if air and oxygenated or Fe^{3+} -rich waters can be excluded from pyrite, its oxidation can be inhibited and little or no acid will be generated. Because the diffusion of O_2 in water is a slow process, and the solubility of O_2 in water is low, the exclusion of atmospheric O_2 from pyrite containing material can significantly reduce the rate of AMD formation.

Microenvironments

The microenvironment characterized by chemical (pH, O_2 , Fe^{3+} , etc.) and physical conditions varies spatially and temporally and determines the quality and quantity of AMD. As a result, acid mine drainage generally is a mixture of fluids from a variety of dynamic microenvironments within the spoil, so that prediction of discharge water quality is difficult and imprecise. Within unsaturated spoil, water typically fills small pores and occurs as films on particle surfaces. Flow rates of the water vary from relatively rapid movement through interconnected large pores, fractures, and joints to slow movement or nearly stagnant conditions in water films or small pores. Also, the abundance and distribution of pyrite and other minerals varies from one particle to another. Volumes with abundant pyrite, free movement of air, and impeded movement of water are expected to develop higher acidities than equal volumes that contain less pyrite or that are completely saturated with water. In addition, *T. ferrooxidans* may attach directly to pyrite surface and create its own microenvironment favorable to oxidation. Because of these factors, the chemical environment within spoil, and

consequently, water quality in unsaturated and saturated spoil commonly exhibit spatial and temporal variability.

Temperature

As any other reaction, the rate of reaction that form AMD increase with increasing temperature, so that AMD is formed faster if the pyritic material is warm. An exception to this trend is the rate of Fe oxidation by *T. ferrooxidans* above about 35°C. These bacteria thrive at optimum temperatures of 25 to 35°C, but they become inactive or die as temperatures increase to about 55°C (Cathles, 1979).

Environmental Consequences of AMD

Acid Mine Drainage (AMD) is the greatest environmental problems of coal mining industry and main source of water pollution in and around mining areas. AMD refers to the water with high concentrations of sulfuric acid draining out of surface or subsurface coalmines. AMD is highly acidic and contains high concentration of dissolved metals and trace elements. Aluminum, calcium and sulphate have been found to be major mine drainage constituents. Trace metals, such as lead, barium, and cadmium are found in low concentrations and form minor constituents of AMD. The AMD discharge, when contaminates water bodies causes serious pollution. Both, active and abandoned coal mines generate AMD and have the potential for long-term, devastating impacts on rivers, streams and aquatic life.

The influx of untreated acid mine drainage into streams can severely degrade both habitat and water quality often producing an environment devoid of most aquatic life and unfit for desired uses. The severity and extent of damage depends upon a variety of factors including the frequency, volume, and chemistry of the drainage, and the size and buffering capacity of the receiving stream. Ferric iron, when discharged to surface water, hydrolyzes to produce hydrated iron oxide and more acidity. The acid lowers the pH of the

water, making it corrosive and unable to support many forms of aquatic life. Acid formation is most serious in areas of moderate rainfall where rapid oxidation and solution of exposed minerals can occur. Various impacts range in severity from isolated nuisance type problems to severe water quality impacts affecting large volumes of groundwater and miles of watercourse. Impacted uses include agricultural (irrigation and livestock), industrial, and potability of water supplies along with recreational uses, scenic resource appreciation, and aquatic organism habitat. Acidic mine drainage in particular can also be toxic to vegetation when recharging to the shallow groundwater system and soil water zones.

In areas where surface and ground waters have been contaminated by acid mine drainage, treatment of water supplies becomes more difficult, more time consuming, and more expensive. The constituents listed below are typically elevated in mine drainage or in groundwater recharged by mine drainage and their properties which can render a domestic water supply unusable without treatment, unpalatable, or aesthetically offensive. Degradation of soil by AMD is a common seen in and around mining area. Agricultural fields receiving AMD become unfit for cultivation due to acidity, metal contamination and deposition of the precipitate of $\text{Fe}(\text{OH})_3$. The soil loses fertility resulting into stunted growth and loss of agricultural productivity (Das Gupta *et al.* 2002; Swer and Singh, 2003)

Constituents of AMD

Iron

The taste threshold of iron in water has been given as 0.1 and 0.2 mg/l of iron from ferrous sulfate and ferrous chloride respectfully. It has been reported that ferrous iron imparts a taste at 0.1 mg/l and ferric iron at 0.2 mg/l. Staining of plumbing fixtures occurs at 0.3 mg/l. Certain animals such as cows are sensitive to minor changes in iron concentration and

do not drink enough water if it is high in iron, and consequently, milk production is affected.

pH

The hydrogen ion concentration can affect the taste of water. At a low pH water tastes sour. The bactericidal effect of chlorine is weakened as pH increases and it is advantageous to keep the pH close to 7. Water with a pH below 7.0 is corrosive to plumbing and can result in constituents such as copper, zinc, cadmium, and lead being dissolved in drinking water.

Sulfate

High sulfate (SO_4^{2-}) level in water contaminated with AMD is a common feature. The concentration of SO_4^{2-} may vary from a few mg/l to 3000–4000 mg/l in AMD. High sulfate levels have laxative effects and cause taste and odor problems.

Total dissolved solids

Excessive total dissolved solid in drinking water is objectionable because of possible physiological effects and unpalatable mineral tastes. Physiological effects include laxative effects, effects on the cardiovascular system, and toxemia associated with pregnancy.

Manganese

Elevated manganese causes several specific problems when encountered in drinking water, such as unpleasant tastes, deposits on food, laundry staining, reduction in water main capacity, and discoloration of porcelain fixtures. Staining may occur at concentrations above 0.5 mg/l.

The concentration of some of the constituents in a typical water sample contaminated with AMD is shown in Table 1.

Table 1: Result of analysis of pH, conductivity, acidity, alkalinity, SO_4^{2-} , Fe, Ca, Mg, and Mn in typical water samples contaminated with AMD

Water sample	pH	Conductivity mS/cm	Acidity CaCO_3	Alkalinity CaCO_3	SO_4^{2-} mg/l	Fe mg/l	Ca mg/l	Mg mg/l	Mn mg/l
1	2.6	2120	688	0	913	174	83	74	26
2	2.4	2980	1080	0	1350	162	97	102	40
3	3.1	3400	1106	0	1904	472	253	169	80
4	2.4	2710	1020	0	988	140	62	56	30
5	2.3	5270	2380	0	2944	586	131	136	48

Impact on Industrial use of Water

The major problem of most industrial water users is corrosion control. As discussed previously, increased acidity has been found to accelerate the corrosion of industrial water-using equipment, navigational equipment, buried transmission lines, and ordinary metal structures such as culverts, bridges, and pumps. Scale formation (incrustation) produced by increased water hardness reduces the heat exchange efficiency of boilers. Elevated iron and manganese concentrations interfere with textile dyeing and metal plating. The water contaminated with AMD is also not suitable for irrigation purposes.

Problems of corrosion of metal structures

Chemical corrosion occurs when a particular constituent is present in water in sufficient concentration to cause rapid removal of material over broad areas. Chemical corrosion can cause severe damage regardless of the amount of total dissolved solids. Damage to plumbing caused by corrosive water represents a major expense to utilities and water users. There are two recognized types of corrosion; chemical and electrochemical. The chemical corrosion takes place due to low pH and associated water problems. However, the electrochemical corrosion is more prevalent and occurs due to a difference in electrical potential on the surface of the metal(s), and water with enough dissolved solids content to act as a

conductor. A difference in electrical potential can occur between two different metals or on the surface of the same metal in areas around joints, machine cuts, exposed threads, or breaks in surface coatings.

Problem of incrustation

Incrustation is another major problem for pumps and associated metal structures. The kind and amount of dissolved minerals and gases in natural waters determine their tendency to deposit mineral matter as incrustation. The major forms of incrustation include; (1) incrustation from precipitation of calcium and magnesium carbonates or their sulfates; (2) incrustation from precipitation of iron and manganese compounds, primarily their hydroxides or hydrated oxides; and (3) plugging caused by slime-producing iron bacteria or other slime-forming organisms. Chemical incrustation usually results from the precipitation of carbonates, principally calcium, from groundwater in the proximity of the well screen. Other substances, such as aluminum silicates and iron compounds, may also be entrapped in the scale like carbonates that cement sand grains together around the screen.

Iron and manganese incrustation is another common problem in pumping wells. During pumping, velocity-induced pressure changes can disturb the chemical equilibrium of the groundwater and result in the deposition of insoluble iron and manganese hydroxides. These hydroxides have the consistency of a gel, and may occupy relatively large volumes; over time, they harden into scale deposits.

Management of AMD

Water plays a key role in the formation and transport of acid mine drainage. It is an essential part of the pyrite oxidation process and necessary for dissolution of neutralizing minerals such as calcite and dolomite. It is also the transport medium for pyrite oxidation and neutralizing products. Therefore, proper management of water in mining area is necessary to ameliorate the problems of AMD. There are at least four

means of managing water on surface coal mines. The first is to minimize infiltration into the spoil surface. A second is to minimize the contact time between groundwater and acid-producing mine spoil. A third is to promote the contact of infiltrating water with calcareous materials in the mine spoil. The fourth is to submerge acid-forming materials below the water table. The water management practices discussed below focus on the control of surface water runoff and infiltration, and groundwater management.

Erosion and sedimentation controls

Although relatively simple, an adequate erosion and sedimentation plan is an essential component of water management on surface mines. Well designed and constructed erosion and sedimentation controls can prevent a significant amount of infiltration into a mine site. The use of erosion and sedimentation controls has been a recommended practice. An erosion and sedimentation control plan generally consists of sedimentation ponds and a network of associated collection and diversion ditches. Specific erosion and sedimentation features used to minimize surface water infiltration on a surface mining site include construction of diversion ditches, collection ditches and sedimentation and treatment ponds.

Diversion ditches are usually located above the final high wall or in areas where it is necessary to divert surface flows away from spoil material. Diversion ditches may not be needed on all mine sites due to topography. Nevertheless, their function to prevent excessive infiltration of surface water into backfilled spoils is often overlooked and should be considered in mine planning. The purpose of collection ditches is to collect runoff (mostly from precipitation) from active or recently backfilled areas and convey it to sedimentation ponds in a non-erosive manner. Collection ditches are normally located in undisturbed ground below the mining area; however, they may at times need to be constructed in relatively permeable spoil material. When constructed in spoil, collection ditches may direct large quantities of water into the backfill. To prevent this, ditches in spoil should be lined with impermeable material to prevent

infiltration. As with collection ditches, *sedimentation and treatment* ponds should be located with regard to possible infiltration of water. If constructed in spoil material and not lined properly, large amounts of infiltration are possible. Ponds should be located in original ground where practical or lined with impermeable material. Experience has shown that it is better to construct ponds in original ground rather than attempting to line them. Ponds to be left as permanent features or in acid mine drainage prone areas should not be constructed in spoil.

Control of surface water infiltration

Reclamation and revegetation can reduce the production of AMD by promoting surface runoff and evapotranspiration, thus minimizing infiltration into the backfilled spoil. Another method to reduce surface water infiltration is the construction of a low-permeability barrier immediately below the topsoil and subsoil. This barrier can be composed of clay or other suitable material such as fly-ash cement (Sheetz *et al.* 1997). Also, other considerations such as slope stability and soil suitability for reclamation must be taken into consideration.

Conclusion

Acid mine drainage can be characterized with low pH, elevated concentrations of sulfate (SO_4), iron (Fe), manganese (Mn) and aluminum (Al) as well as common elements such as calcium, sodium, potassium and magnesium. The pH is most commonly either in the ranges 3 to 4.5 or 6 to 7, with fewer intermediate or extreme values. A key parameter is the acidity, which is the amount of base required to neutralize the solution. In coal mine drainage, major contributors to acidity are from ferrous and ferric Fe, Al, and Mn, as well as free hydrogen ions. Acidic mine drainage is formed by the oxidation of pyrite to release dissolved Fe^{2+} , SO_4^{2-} and H^+ , followed by the further oxidation of the Fe^{2+} to Fe^{3+} and the precipitation of the iron as a hydroxide or similar substance, producing more H^+ . Neutralization of the acidic solution by limestone or similar

materials can form neutral mine drainage with high SO_4 and possibly elevated Fe and Mn.

Many factors control the rate and extent of AMD formation in surface coal mines. More abundant pyrite in the overburden tends to increase the acidity of drainage, as does decreasing grain size of the pyrite. Iron-oxidizing bacteria and low pH values speed up the acid-forming reaction. Rates of acid formation tend to be slower if limestone or other neutralizers are present. Access of air containing the oxygen needed for pyrite oxidation is commonly the limiting factor in rate of acid generation. Both accesses of air and exposure of pyrite surfaces are promoted by breaking the pyrite-bearing rock. The oxygen can gain access either by molecular diffusion through the air-filled pore space in the spoil, or by flow of air which is driven through the pore space by temperature or pressure gradients.

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