1.0 ACID MINE DRAINAGE

1.1 Formation

Acid mine drainage (AMD) or acid rock drainage, collectively called acid drainage (AD), is formed when certain sulfide minerals in rocks are exposed to oxidizing conditions. Much of the AD worldwide is commonly thought to be associated with coal mining, but AD can occur under natural conditions or where sulfides in geologic materials are encountered in metal mining, highway construction, and other deep excavations. Iron sulfides common in coal regions are predominately pyrite and marcasite (FeS_2), but other metals may be combined with sulfide in the form of chalcopyrite ($CuFeS_2$), covellite (CuS), and arsenopyrite (FeAsS) (Table 1.1). Pyrite commonly occurs with other metal sulfides, potentially causing AD.

Table 1.1. Some important metal sulfides which occur in mining regions. The predominant acid producers are pyrite and marcasite.

FeS_2 -	pyrite	MoS_2 -	molybdenite
FeS_2 -	marcasite	NiS -	millerite
Fe_xS_x -	pyrrhotite	PbS -	galena
Cu_2S -	chalcocite	ZnS -	sphalerite
CuS -	covellite	FeAsS -	arsenopyrite
CuFeS2 -	chalcopyrite		

Upon exposure to oxidizing conditions and in the absence of alkaline materials, some sulfide minerals are oxidized in the presence of water and oxygen to form highly acidic, sulfate-rich drainage. Acidity levels, and metal composition and concentration depend on the type and amount of sulfide mineral and the presence or absence of alkaline materials. In the coal fields when sulfides are present, the oxidation of Fe disulfides and

subsequent conversion to acid occur through several reactions. The following four chemical equations are accepted to explain the processes (Stumm and Morgan 1996).

Equation 1.1 $FeS_2 + 7/2\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

Equation 1.2 $Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + ½\ H_2O$

Equation 1.3 $Fe^{3+} + 3\ H_2O = Fe(OH)_3 + 3\ H^+$

Equation 1.4 $FeS_2 + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$

In equation 1.1, Fe sulfide is oxidized, thereby releasing ferrous iron (Fe^{2+}, the reduced form of iron), sulfate (SO_4^{2-}), and acid. Ferrous iron in equation 1.2 can be oxidized to form ferric iron (Fe^{3+}). Ferric iron can then either be hydrolyzed and form ferric hydroxide, $Fe(OH)_3$, and H^+ acidity (equation 1.3), or it can directly attack pyrite and act as a catalyst in generating much greater amounts of ferrous iron, sulfate, and acidity (equation 1.4).

If any of the processes represented by the equations were slowed or altogether stopped, the generation of AMD would also slow or cease. Removal of air and/or water from the system, two of the three principal reactants, would stop pyrite from being oxidized. Almost complete absence of oxygen occurs in nature when pyrite is found beneath the water table where oxidizing conditions are limited. Under these conditions, the pyrite remains almost completely unreacted. When pyrite is enclosed within massive rock, only minimal amounts of pyrite are oxidized through natural weathering, thereby generating only small amounts of acid, and this acid is sometimes naturally diluted or neutralized by surrounding alkaline rocks. However, when large volumes of pyritic material are fractured and exposed to oxidizing conditions, which can occur in mining or other major land disturbances, the pyrite reacts, and water dissolves and moves the reaction products (Fe and other metals, sulfate, and acid) into ground and surface water sources.

Under many conditions, equation 1.2 is the rate-limiting step in pyrite oxidation because the conversion of ferrous iron to ferric iron is slow at pH values below 5 under abiotic conditions (Singer and Stumm 1968, 1970). However, Fe-oxidizing bacteria, principally Thiobacillus, greatly accelerate this reaction, so the activities of bacteria are crucial for generation of most AMD (Leathen et al. 1953, Waksman 1922), and much work in bactericides has been conducted. In contrast, availability of oxygen may be the rate-limiting step in spoil of low porosity and permeability such as that composed of soft shale, so that oxidation is limited to the upper few meters of spoil. In porous and permeable spoil composed of coarse sandstone, air convection driven by the heat generated by pyrite oxidation may provide high amounts of oxygen deep into the spoil (Guo et al. 1994, Guo and Cravotta 1996).

1.2 Forms of Sulfur in Rock

Sulfur in coal and rocks associated with coal mines can occur as organic sulfur, sulfate sulfur, and pyritic sulfur. Some sulfur in coal appears to have been introduced after the peat had been converted to coal, as is evidenced by pyrite coatings on vertical fracture surfaces, called cleat, in the seam. Much of the pyrite present in rocks and overburdens of coal mines occurs as very small crystalline grains intimately mixed in sandstones and shales (Temple and Koehler 1954). The origin of sulfur in large concretions, nodules, lenses, bands, and fillings in porous layers of coal is less well understood (U.S. Geological Survey 1968).

Organic sulfur is believed to be complexed and combined with organic constituents of coal and organically bound within the coal. This form of sulfur is only found in appreciable quantities in coal beds and in other carbonaceous rocks. Generally, the organic sulfur component is not chemically reactive and has little or no effect on acid-producing potential.

Sulfate sulfur is usually only found in minor quantities in fresh coal and other undisturbed pyrite-containing rocks, and is commonly the result of weathering and recent oxidation of sulfide sulfur. Some sulfate minerals like jarosite ($KFe_3(SO_4)_2(OH)_6$) can dissolve and form acid solutions in near surface environments.

Pyritic or sulfide sulfur is the dominant form of sulfur in the majority of coal and associated rocks. It is the sulfur form of greatest concern. Of all the sulfide minerals that may be present, Fe disulfides predominate and are the major acid producers. Accordingly, the maximum potential acidity (MPA) of a fresh overburden sample correlates closely with the pyritic sulfur content. Studies have shown that variations in total sulfur contents of overburden samples reflect similar variations in pyritic sulfur content. Several types of pyritic sulfur are known based on physical appearance, and they are classed into six groups:1) primary massive, 2) plant replacement pyrite, 3) primary euhedral pyrite, 4) secondary cleat (joint) coats, 5) mossy pitted pyrite, and 6) framboidal pyrite. Caruccio et al. (1988) provide an extensive review of the different forms, morphologies, and reactivity of pyritic materials.

The equations for pyrite oxidation show that a material containing 1% sulfur, all as pyrite, would yield upon complete reaction an amount of sulfuric acid that requires 31.25 Mg of $CaCO_3$ to neutralize 1000 Mg (or tons/1000 tons) of the material (Sobek et al. 1978). When sulfur in the rock is exclusively pyrite, the total sulfur content of the rock accurately quantifies the acid-producing potential, if it were all to react. When organic or sulfate sulfur are present in significant amounts in partially weathered rocks, total sulfur measurements overestimate the amount of acid that will be formed upon oxidation. Therefore, correction for sulfates and organic sulfur naturally present in some overburdens or resulting from partial weathering of pyritic materials may be necessary to increase accuracy in predicting the acid-producing potential of materials containing mixed sulfur species.

The rate of pyrite oxidation depends on numerous variables such as:

- reactive surface area of pyrite (Singer and Stumm 1968),
- form of pyritic sulfur (Caruccio et al. 1988),
- oxygen concentrations (Smith and Shumate 1970),
- solution pH (Smith and Shumate 1970),
- catalytic agents (Caruccio et al. 1988),
- flushing frequencies (Caruccio et al. 1988),
- the presence of Thiobacillus bacteria (U.S. Environmental Protection Agency 1971).

The possibility of identifying and quantifying the effects of these and other controlling factors with all the various rock types in a field setting is unlikely. A variety of approaches to evaluating the rate are discussed in the following pages.

1.3 Alkalinity in Rocks

The natural base content of overburden materials (alkali and alkaline earth cations, commonly present as carbonates or exchangeable cations on clays) is important in evaluating the future neutralization potential (NP) of the materials. The amount of alkaline material in unweathered overburden may be sufficient to equal or overwhelm the acid-producing potential of the material. Of the many types of alkaline compounds present in rocks, carbonates (specifically calcite and dolomite) are the primary alkaline compounds which occur in sufficient quantities to be considered as effective deterrents to AMD generation.

In overburden containing both alkaline and pyritic material, the alkaline material may be sufficient to reduce oxidation from occurring or to neutralize the acid formed from pyrite. Higher alkalinities also help control bacteria and restrict solubility of ferric iron, which are both known to accelerate acid generation. Although a number of factors must be considered, a balance of the acid-producing potential and neutralizing capacity of an overburden sample will indicate whether acidity or alkalinity is expected in the material upon complete weathering (Caruccio and Geidel 1980).

1.4 Acid Mine Drainage

AMD is an acidic, iron and sulfate water that forms under natural conditions when geologic strata containing pyrite are exposed to the atmosphere or oxidizing environments. AMD can form from coal mining, both in surface and in underground mines. Alkaline mine drainage is water that has a pH of 6.0 or above, contains alkalinity, but may still have dissolved metals that can create acid by reactions 1.2 and 1.3. The drainage quality (acid or alkaline) emanating from underground mines or backfills of surface mines is dependent on the acid (sulfide) and alkaline (carbonate material) minerals contained in the disturbed geologic material. In general, sulfide rich and carbonate poor materials are expected to produce acidic drainage. In contrast, alkaline rich materials, even with significant sulfide concentrations, often produce net alkaline water.

Mine drainage can be categorized into several basic types (Skousen and Ziemkiewicz 1996): Type 1 mine drainage has little or no alkalinity (pH <4.5) and contains high concentrations of Fe, Al, Mn, and other metals, acidity, and oxygen. This type of water is called AMD. AMD may also refer to water that has a pH <6.0, and contains net acidity (acidity is greater than alkalinity).

Type 2 mine drainage has high total dissolved solids containing high ferrous iron and Mn, no or low oxygen content, and pH >6.0. Upon oxidation, the pH of this water drops dramatically and becomes Type 1 AMD.

Type 3 mine drainage has moderate to high total dissolved solids, low to moderate ferrous iron and Mn, no or low oxygen content, pH >6.0, and alkalinity greater than acidity (commonly called alkaline mine drainage). Upon oxidation, the acid generated from metal hydrolysis and precipitation reactions are neutralized by alkalinity already present in the water.

Type 4 mine drainage is neutralized AMD with pH >6.0 and high total suspended particulates. Settling of metal hydroxides in the water has not yet occurred. With residence time in a pond, the particulates will settle out and form Type 5 water.

Type 5 water is neutralized AMD, with pH >6.0 and high total dissolved solids. After most metal hydroxides have precipitated in a settling pond, the main cations left in high concentrations in the water are usually dissolved Ca and Mg. Soluble oxy-anions like bicarbonate and sulfate also remain in solution. If alkalinity or oxygen is lacking in the neutralization process, the water will not reach Type 5.

Another type of mine drainage occurs from mines with minor sulfides and low to moderate amounts of carbonate. The water typically is near neutral pH, the specific conductance is low (<100 uS/mm) and acidity and alkalinity are nearly balanced. These are classified as inert or neutral waters.

Mixing among these various types of waters creates transitional types of water, so adequate sampling and analysis of the pH, oxygen status, and metal concentrations is important to determine the type of mine drainage and the intensity of its acidic character.

1.5 Discharge Limits

Coal mine operators are required to meet environmental land reclamation performance standards established by federal (the Surface Mining Control and Reclamation Act, SMCRA) and state regulatory programs. Operators must also meet water quality standards established in the Clean Water Act of 1972 (CWA), which regulates discharges into waters of the U.S. Control of AMD is a requirement imposed on operators by both SMCRA and CWA. In addition to the surface mining permit, each mining operation must be issued a National Pollutant Discharge Elimination System (NPDES) permit under the CWA. Allowable pollutant discharge levels are usually determined by the U.S. Environmental Protection Agency's (EPA) technology-based standards, or the discharge levels may be based on the more stringent water quality-based standards where discharges are being released into streams with designated uses. NPDES permits on surface mines usually require monitoring of pH, total suspended solids (TSS), Fe and Mn concentrations. Other parameters may be required by the regulatory authority to address specific concerns in a particular mining situation.

1.6 Acidity and Alkalinity Measurements

Acidity and alkalinity can be measured in various units such as equivalents/L, milliequivalents/L, mg/L as $CaCO_3$, and mg/L as HCO_3^- (Eaton et al. 1995). In this document, mg/L as $CaCO_3$ will be used as the unit for acidity and alkalinity. Acidity is a measure of the amount of base needed to neutralize a volume of water. For AMD, the acidity should be measured by a "hot acidity" procedure that oxidizes Fe^{2+} and Mn^{2+} so that their acid character is correctly measured. Acidity in AMD is comprised of mineral acidity (Fe, Al, Mn, and other metals depending on the specific metal sulfide exposed during disturbance) and hydrogen ion acidity. Other metals in AMD vary widely, but AMD is characterized by low pH, high sulfate and Fe. As contaminated streams flow into larger uncontaminated streams or lakes, dilution occurs. Also, natural chemical and biological reactions cause some neutralization of acidity and precipitation of metals. In studies of uncontaminated natural water, the term acid water commonly refers to water with low pH. For example, waters contaminated from "acid rain" usually have low pH (from 3.5 to 4.5), but have very little mineral acidity.

Drainage from metal mines (acid rock drainage) may contain significant amounts of Zn, Cu, Ni, Pb, etc. However, when dealing with AMD from coal mines in the eastern U.S., the pH, Fe, Al, and Mn usually account for the majority of the acidity (Hedin et al. 1991). Acidity can also be estimated for acid rock drainage from metal mines by incorporating additional metals into the equation, and by knowing their concentrations, their molecular weights, and valences.

As an example, acidity of coal mine drainage can be estimated by using metal concentrations in the following manner:

$$\text{Estimated Acidity} = 50\ (2\ Fe^{2+}/56 + 3\ Fe^{3+}/56 + 3\ Al^{3+}/27 + 2\ Mn^{2+}/55 + 1000(10^{-pH}))$$

where estimated acidity is expressed as mg/L $CaCO_3$ equivalent, all metal concentrations are in mg/L, and 50 transforms milliequivalents (meq) of acidity into mg/L $CaCO_3$ equivalent. For AMD with a pH <4.5 (no alkalinity present), this equation can be used to estimate the actual titrated, laboratory measured acidity of the water.

For example, a water sample was measured to have an acidity value of 410 mg/L as $CaCO_3$, pH of 3.1, ferrous iron (Fe^{2+}) content of 14 mg/L, ferric iron (Fe^{3+}) of 33 mg/L, Al of 47 mg/L, and Mn of 9 mg/L. Substituting the ion concentrations into the equation above, the milliequivalents (meq) of each ion are: hydrogen ion is 0.8, ferrous iron is 0.5, ferric iron is 1.77, Al is 5.22, and Mn is 0.33. These ions total 8.62 meq. Multiplying by 50 gives 431 mg/L of acidity as $CaCO_3$. This calculated value is close to the laboratory measured value of 410 mg/L as $CaCO_3$.

Additional metals such as Pb, Cu, Zn and Ni may furnish acidity, but the amount depends on their concentration, the specific solid that is precipitated, and the anion composition of the solution. For example, the precipitation of $PbSO_4$ from a sulfate rich AMD generates no acidity; precipitation of $PbCO_3$ produces 1 H^+ per Pb^{2+}, and PbO precipitation would generate 2 H^+. Precipitation of ZnO in principle produces 2 H^+ but is not complete at pH 8.3, which is where the acidity titration is usually measured. Unless these metals are present in high concentrations (tens of mg/L), they are probably not significant in estimating acidity.

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