

# Acid Mine Drainage

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Acid mine drainage (AMD) has been a detrimental by-product of coal mining for many years. At present, acid mine drainage continues to pose a potential problem in some areas, despite improved prediction and prevention techniques.

### **Acid Mine Drainage Research**

Acid mine drainage (AMD) has been the subject of intensive research since the 1960's. Research efforts have proceeded recently through the [Acid Drainage Technology Initiative](#). The major areas of research on AMD are [Prediction of AMD](#) and [Prevention/Mitigation](#).

The following is an overview of information on some major acid mine drainage topics.

#### **Factors controlling formation of AMD**

The formation of acid drainage is a complex geochemical and microbially mediated process. The acid load ultimately generated from a minesite is primarily a function of the following factors:

#### **Chemistry of Pyrite Weathering**

[Microbiological Controls](#)

[Depositional environment](#)

[Acid/base balance of the overburden](#)

[Lithology](#)

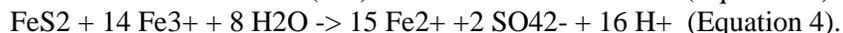
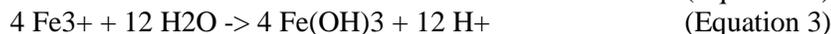
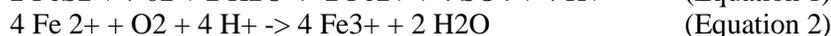
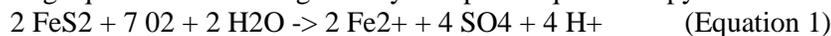
[Mineralogy](#)

[Minesite hydrologic conditions](#)

#### **Chemistry of Pyrite Weathering**

A complex series of chemical weathering reactions are spontaneously initiated when surface mining activities expose spoil materials to an oxidizing environment (Deutsch, 1997). The mineral assemblages contained in the spoil are not in equilibrium with the oxidizing environment and almost immediately begin weathering and mineral transformations. The reactions are analogous to "geologic weathering" which takes place over extended periods of time (i.e., hundreds to thousands of years) but the rates of reaction are orders of magnitude greater than in "natural" weathering systems. The accelerated reaction rates can release damaging quantities of acidity, metals, and other soluble components into the environment. The pyrite oxidation process has been extensively studied and has been reviewed by Nordstrom (1979). For purposes of this description, the term "pyrite" is used to collectively refer to all iron disulfide minerals.

The following equations show the generally accepted sequence of pyrite reactions:



In the initial step, pyrite reacts with oxygen and water to produce ferrous iron, sulfate and acidity. The second step involves the conversion of ferrous iron to ferric iron. This second reaction has been termed the "rate determining" step for the overall sequence.

The third step involves the hydrolysis of ferric iron with water to form the solid ferric hydroxide (ferrihydrite) and the release of additional acidity. This third reaction is Ph dependent. Under very acid conditions of less than about Ph 3.5, the solid mineral does not form and ferric iron remains in solution. At higher Ph values, a precipitate forms, commonly referred to as "yellowboy."

The fourth step involves the oxidation of additional pyrite by ferric iron. The ferric iron is generated by the initial oxidation reactions in steps one and two. This cyclic propagation of acid generation by iron takes place very rapidly and continues until the supply of ferric iron or pyrite is exhausted. Oxygen is not required for the fourth reaction to occur.

The overall pyrite reaction series is among the most acid-producing of all weathering processes in nature.

### Microbiological Controls

The pyrite weathering process is a series of chemical reactions, but also has an important microbiological component. The conversion of ferrous to ferric iron in the overall pyrite reaction sequence has been described as the "rate determining step" (Singer and Stumm, 1970). This conversion can be greatly accelerated by a species of bacteria, *Thiobacillus ferrooxidans*. This bacteria and several other species thought to be involved in pyrite weathering, are widespread in the environment. *T. ferrooxidans* has been shown to increase the iron conversion reaction rate by a factor of hundreds to as much as one million times (Singer and Stumm, 1970; Nordstrom, 1979).

The activity of these bacteria is Ph dependent with optimal conditions in the range of Ph 2 to 3. Thus, once pyrite oxidation and acid production has begun, conditions are favorable for bacteria to further accelerate the reaction rate. At Ph values of about 6 and above, bacterial activity is thought to be insignificant or comparable to abiotic reaction rates. The catalyzing effect of the bacteria effectively removes constraints on pyrite weathering and allows the reactions to proceed rapidly. The role of microbes in pyrite oxidation is described in more detail by Kleinmann and others (1981) and Nordstrom (1979).

### Depositional Environment

Paleoenvironments under which coal bearing rocks formed can be characterized into three general categories: marine; freshwater; and brackish. Studies of Pennsylvanian age coal bearing rocks have shown that paleoenvironment can be used to broadly define acid drainage potential (Skousen and others, 1998, Brady and others 1988; Hornberger and others 1981). Rocks formed in brackish water conditions are generally most prone to acid production; freshwater systems usually produce non-acid water, and marine systems produce variable drainage quality. In some coal measures, the paleoenvironment varies laterally and vertically within a single minesite and is a controlling factor in the inherent distribution of pyrite and carbonates.

### Acid/Base Balance and Reaction Rates

Drainage and spoil quality is a product of two competing processes: acid formation from pyrite oxidation, and generation of alkalinity from dissolution of carbonates and other basic minerals.

The acid generation process consists of three phases: initiation; propagation; and termination. The initiation phase can begin as soon as pyritic materials are exposed to an oxidizing environment, however, the acid load generated is relatively small. In the propagation phase, acid production increase rapidly. In the termination phase, acid production gradually declines. The actual times associated with these phases are, at present, ill-defined, but appear to be on the order of years to decades. Modeling predictions and comparison to a limited number of field sites indicate the peak acid load occurs 5 to 10 years after mining, followed by a gradual decline over 20 to 40 years (Ziemkiewicz and others, 1991, Hart and others, 1991). The same studies project very long decay curves for coal refuse (beyond 50 years) before acid leachate is depleted. Reliable acid generation/depletion predictions for underground mine discharges are not available.

The overall acid-producing process can proceed very rapidly with few chemical constraints. In contrast, dissolution or reaction rates of many common minerals is generally slow due to solubility limitations. Production of alkalinity tends to attain a constant value or level off with time so that the rate of acid production commonly may exceed the production of alkalinity.

The trends in reaction rates can be offset or enhanced by the mass balance between acid and alkaline producing minerals. A general relation between acid and basic minerals and resultant drainage quality is described as follows:

- o Low pyrite, low base content - Drainage may contain low levels of acidity, or maybe non-acid. Low concentrations of dissolved metals.

- Low pyrite, high base content - Drainage is alkaline with low concentrations of dissolved metals.
- High pyrite, low base content - Drainage is acid with high concentrations of dissolved metals.
- High pyrite, high base content - Drainage is usually alkaline, occasionally acid, with high concentrations of dissolved metals.

The conditions most conducive to acid formation are high pyrite contents with little base material present. Conversely, an excess of base relative to pyrite is most likely to preclude acid formation. Sites containing low quantities of pyrite and bases produce the most variable drainage quality and are the most difficult to assess with premining predictive techniques.

### Lithologic Controls

Lithology or rock type also influences spoil and drainage quality. Physical characteristics of the rock, such as porosity, and accessory minerals can exert various constraints or enhancements to the overall chemical weathering process. For example, pyritic sandstones tend to release their acid load rapidly (Ziemkiewicz, 1991). Argillaceous rocks tend to release their acid load over a longer period of time. Accessory minerals (clays and other silicates) may dissolve, form new minerals, or attenuate the acid and alkaline weathering products.

### Mineralogical Controls

The mineral pyrite occurs in several different morphological forms and a range of grain sizes. The "framboidal" form is considered highly reactive and is characterized by a small grain size and large surface area (Caruccio and others, 1977). Pyrite can occur in grain sizes ranging from invisible to the eye up to several inches. Framboids and other fine grained pyrites with a large surface area are much more chemically reactive than the coarser forms (Evangelou, 1995). The reactivity of fine grained pyrites reflects the fact that acid generating reactions occur at the mineral surface.

### Minesite Hydrologic Conditions

Minesite hydrology plays a critical role in determining drainage quality, yet the flow mechanics of ground water in spoils are among the least understood aspects of AMD. The products of pyrite oxidation are free acid and soluble acid salts. If no percolating waters are present, the acid salts generated from the limited available moisture simply reside within the spoil. When excess moisture is present, the acid weathering products are dissolved and transported with the water moving through the material.

The chemistry of ground-water discharges can vary depending on the degree of flushing (Snyder and Caruccio, 1988) and time since the last precipitation event. Ground-water discharge can be "flashy" or rapid shallow interflow associated with high intensity short duration precipitation events or base flow. Underground mine discharges which drain from large volume pool storage typically exhibit a muted or seasonal response to precipitation patterns.

The position of a water table within the spoil also influences drainage quality. Water table elevations in spoils fluctuate in response to seasonal conditions forming a zone of cyclic wetting and drying. This provides optimal conditions for the oxidation and subsequent leaching of pyrite and associated weathering products. Ground-water flow paths and the location and elevation of saturated zones are often difficult to predict in mine spoils.

Numerous chemical, physical and biological factors interact to control the quality of mine drainage. Although the basic processes of acid mine drainage formation are universal, the importance of any single controlling factor is frequently specific to minesite conditions.

### **Prediction of AMD**

Prediction of acid generation based on geochemical analysis has been practiced for about 25 years. The most widely used method, Acid/Base Accounting (Sobek and others, 1978), quantitatively balances pyrite against carbonates and other alkaline materials. Its original use was to identify topsoil substitutes and root zone media, not a quantitative predictor of drainage quality. As a water quality predictor, it has been accurate in some instances and misleading in others (Erickson and Heiden, 1988). Research has therefore, continued on improving predictive methods.

A variety of simulated weathering tests have been developed and studied as drainage quality predictors (Caruccio, 1967; Sturey and others, 1982; Renton and others, 1988) Test details differ, but all methods attempt to mimic cyclic wetting/drying and flushing of spoil piles. Currently, there is no consensus on which method most accurately reflects field conditions. Questions have also arisen regarding length of laboratory test time and extrapolation to field weathering time.

It has been observed that pyrites of different origins can exhibit varying levels of reactivity. Laboratory studies have been conducted (Hammack and others, 1988) to determine why certain pyrites are more chemically reactive. "Evolved gas analysis," which involves the thermal decomposition of sulfur compounds under controlled conditions, has been used to characterize pyrite reactivity. The basic premise is that lower temperature decomposition reflects unstable and more reactive pyrite. Current research efforts (Sheetz, 1990) are focused X-ray diffraction studies of subtle differences in crystal structure and possible trace inclusions in the crystal lattice, in combination with evolved gas analysis. The goal of these research efforts is to identify the controlling factors and develop a reproducible test that discriminates reactive and nonreactive pyrites.

Computer models are another approach to prediction of acid generation. Most of these models incorporate a number of chemical and physical parameters to describe the chemical reactions of acid generation, microbial catalysis and leaching (transport) of the weathering products (Jaynes, 1991; Scharer and others, 1991). Many of these parameters are difficult to measure or must be estimated and verification is generally lacking. One model uses a "lumped variable" approach, rather than a large number of individual parameters (Rymer and others, 1990; Hart and others, 1991). One combined variable estimates acid generation, and a second variable accounts for leaching of weathering products. This model is still undergoing testing and verification.

### **Prevention/Mitigation of AMD**

Research on acid prevention and mitigation has focused on three main areas: chemical inhibition of the acid generating reactions; inhibition of the microbes responsible for catalyzing the acid generating reactions; and physical or geotechnical treatments to minimize water contact and leaching.

### **Chemical Methods:**

#### Alkaline Addition

Alkaline placement strategies involve either mixing directly with pyritic material or concentrated placement to create a highly alkaline environment. Direct mixing places alkaline materials in intimate contact with pyritic spoil to inhibit acid formation and neutralize any generated acidity in situ. Alkaline addition case studies has been reported by Brady and others, 1990. "Alkaline recharge" employs trenches loaded with alkaline material, usually a combination of soluble sodium carbonate and crushed limestone.

The strategy is to charge infiltrating waters with high doses of alkalinity sufficient to overwhelm any acid produced within the backfill. This approach is highly dependent on the placement of the alkaline trenches to provide maximum inflow to the acid producing zones. An alkaline recharge case study has been reported by Caruccio and Geidel (1989). A third variant of the alkaline placement technique is encapsulation with alkaline material above and below the acid-producing zone.

### **Alkaline Agents**

The benefits of adding lime (calcium carbonate) and other alkaline agents have long been recognized in mitigating acid drainage. However, the complex chemistry of spoil materials has given varying levels of effectiveness in alkaline addition studies.

Direct mixing and contact with pyritic materials appears most effective but an optimum lime to pyrite ratio remains unknown.

Indirect treatments such as alkaline recharge (Caruccio and Geidel, 1989) and borehole injection (Aljoe and Hawkins, 1991; Ladwig and others, 1985) have also yielded mixed results. Field studies of alkaline addition (Brady and others, 1990) have been conducted but it has been difficult to identify definitive cause and effect relationships. Further research is continuing in this area.

### **Phosphate**

The application of rock phosphate is another technique under study as a pyrite oxidation inhibitor (Renton and others, 1988; Evangelou and others, 1991). Pyrite weathering ultimately produces free ferric iron which acts to oxidize additional pyrite, thus establishing a cyclic and self-propagating series of reactions. Dissolution of rock phosphate in acid media releases highly reactive phosphate ions, which will combine with iron to form insoluble iron phosphate compounds. The formation of insoluble iron phosphates would halt or inhibit the cyclic reaction of iron and pyrite. Phosphate treatment has effectively reduced acid generation in laboratory studies; one field study showed a reduction of about seventy percent in acid load compared to a control (Meek, 1991). For reasons not yet completely understood, an application rate of about two to three percent rock phosphate provides the most effective control. Thorough mixing of phosphate and pyritic material also appears necessary for effective treatment. Further research is continuing in this area.

### **Coatings and Sealants**

Other ongoing research activities are focusing on the surface chemistry of pyrite and development of various types of sealers, coatings and inhibitors to halt acid production.

### **Biological Agents/Bactericides:**

The catalytic role of bacteria in pyrite oxidation has been well documented (Kleinmann and others, 1981). Many compounds have been screened as selective bactericides and the anionic surfactants sodium lauryl sulfate and alkyl benzene sulfonate are considered to be the most reliable inhibitors. Application of bactericides has reduced acid loading in field experiments. Bactericides are generally water soluble and will leach from the spoil. Currently, the time

required for leaching of bactericides is uncertain. It is also unclear whether the sulfur and iron oxidizing bacteria will repopulate the spoil and catalyze the acid-producing reactions when the bactericide is depleted.

## **Physical or Geochemical Treatments:**

### Controlled Placement

Controlled placement (special handling) is a preventative measure involving the placement of pyritic or alkaline material during mining to minimize or neutralize the formation of AMD. According to the generally accepted chemical equations for pyrite oxidation, oxygen and water are necessary to initiate acid formation. Exclusion of either reactant should preclude or inhibit acid production. Placement of pyritic material encompasses either an attempt to exclude oxygen, usually by complete submergence below the water table; or an attempt to isolate the material from water contact to avoid leaching of acid salts. Placement of alkaline materials has a twofold role:

1. inhibition of the acid-forming reactions by maintaining neutral to alkaline pH; and
2. neutralization of any acid formed.

### **Submergence**

Submergence relies on several physico-chemical phenomena for success. Oxygen diffuses very slowly and has limited solubility in water. For this approach to succeed, a stagnant or no flow condition and relatively thick saturated zone appears critical. Stagnant flow conditions leading to the development of anoxic (oxygen free) conditions and a saturated thickness on the order of several tens of feet appear to effectively curtail oxygen diffusion. This approach is most successful in large mines in flat terrain where ground-water gradients are low, the saturated zone is thick, and aquifers are of large areal extent. Hammack and Watzlaf (1990) concluded that a water cover to maintain oxygen below a partial pressure of one percent is necessary to inhibit pyrite oxidation.

Submergence is generally not used in the hilly terrain of Appalachia, where gradients and flow velocities are too great to achieve stagnant, anoxic conditions. In these situations, submergence may be counterproductive and actually enhance the production and leaching of acid products. Submergence or flooding is also applied to prevent AMD from underground mines. Key considerations include:

- Whether the mine is located above or below drainage.
- The ability of mine seals and outcrop barriers to prevent seepage.
- Potential for mine seals and outcrop barriers to fail under hydraulic pressure.

In general, flooding to prevent AMD is believed to be more successful in below drainage mines. It is assumed that complete flooding eliminates oxygen and halts or severely curtails acid generation, the mine pool is stable and little or no discharge occurs (Kim and others, 1982). Flooding of above drainage mines is also practiced typically through the use of "wet" seals, which allow water to drain but exclude air entry. Kim and others, 1982 concluded that sealing and flooding above drainage mines does reduce acid loading but is technically more difficult and less effective than other methods in AMD prevention. Monitoring studies of sealed mines indicate a general decrease in pollutant loading 10 to 25 years after mining (Borek and others, 1991), but it is unclear if the decreases were due to mine sealing or "natural phenomena". While

pollutant loading decreased, water quality remained well outside accepted water quality standards for mine drainage.

OSM's rules do not specifically address criteria for outcrop barrier thickness for flooding underground works. A consensus "standard" engineering design approach to outcrop barriers and seals is also lacking. A contract report to the U.S. Bureau of Mines (Dames and Moore, 1981) discusses the factors affecting stability of outcrop barriers. Outcrop barriers should be wide enough to prevent seepage and have sufficient overburden to prevent failure (blowout). Curtain grouting, relief wells and compartmentalized barriers are several of the techniques suggested for controlling AMD discharges.

### **Isolation Above the Water Table**

Placement of pyritic material above a water table is an attempt to isolate the material from contact with water, and preclude leaching of acid weathering products. Compaction and capping with clay or other materials may be also be employed to reduce permeability. In practice, it has proven very difficult to completely isolate spoil materials from water contact. Clay caps and other flow barriers are prone to leakage, and the sporadic infiltration of rain or snowmelt may periodically leach the spoil. The capping approach can be extended to complete encapsulation on top, bottom and sides as a further effort to isolate the materials from water contact. Skousen and others, 1987 give a general review of isolation and capping and other preventive techniques for handling pyritic spoil.

### **Encapsulation/Physical Barriers**

Techniques to isolate or encapsulate pyritic material include the use of fly-ash, cements, bentonite, and other clays; these are a few of the materials studied as sealants and flow barriers by Skousen and others (1987) and Bowders and Chiado (1990). Successful application of these methods in the field is heavily dependent on good engineering and construction practices and site conditions. Other investigations have attempted borehole injection to isolate buried pyritic material. Research is ongoing in this area and may escalate as solid waste disposal rules become more stringent.

### **Water Management**

Water management strategies both during and after mining are another option for reducing acid generation. Water management can include the following:

- Active mining operations can incorporate diversions to route surface drainage away from pyritic material or through alkaline material.
- Spoil material can be placed and rough graded to prevent ponding and subsequent infiltration.
- Prompt removal of pit water can lessen the amount and severity of acid generated.
- Polluted pit water can be isolated from non-contaminated sources (no commingling) to reduce the quantity of water requiring treatment.
- Constructed underdrain systems can be used to route water away from contact with acid forming material.

Special handling (controlled placement), alkaline placement and water management strategies alone or in combination can substantially reduce or mitigate generation of acid drainage. Optimal strategies are site-specific and a function of geology, topography, hydrology, mining method and cost effectiveness.

### **Mine-spoil Hydrology**

Although sometimes not considered an AMD research topic, mine spoil hydrology plays a crucial role in determining drainage quality. Relatively few studies of hydrogeologic processes have been conducted in the context of controlling mine drainage quality, and it is a subject in need of further investigation. Much useful research has been conducted in predictive and preventative acid drainage techniques. No universally effective technologies have yet been developed, however.

### **Treatment Methods and Costs**

The least costly and most effective method of controlling Acid Mine Drainage is to prevent its initial formation. This usually can be accomplished by application of the principles and procedures described in the previous section and careful mine planning.

On occasion, despite the application of sound mining and reclamation principles, Acid Mine Drainage will be formed and must be treated to meet existing Federal and State standards before it is released from the minesite. Prior to opening the mine the operator should evaluate the potential for creating Acid Mine Drainage that would require treatment and should become familiar with the extent of the costs that such treatment might impose. Consideration should also be given to the possibility that treatment might have to be continued well into the future, specifically until such time that the discharge meets effluent standards without treatment.

Treatment, as normally applied to Acid Mine Drainage, involves chemical neutralization of the acidity followed by precipitation of iron and other suspended solids. Treatment systems include:

1. equipment for feeding the neutralizing agent to the Acid Mine Drainage
2. means for mixing the two streams (Acid Mine Drainage and neutralizing agent)
3. procedures for ensuring iron oxidation
4. settling ponds for removing iron, manganese, and other co-precipitates

A number of factors dictate the level of sophistication of the treatment system that is necessary to ensure that effluent standards will be met. These factors include: the chemical characteristics of the Acid Mine Drainage, the quantity to be treated, climate, terrain, sludge characteristics, and projected life of the plant. The chemicals usually used for Acid Mine Drainage treatment include limestone, hydrated lime, soda ash, caustic soda, and ammonia. The following discussion highlights some of the characteristics of each of these neutralizing agents.

#### **Limestone (calcium carbonate)**

Calcium content of limestone should be as high as possible. (Dolomitic limestones are less reactive and generally ineffective in treating Acid Mine Drainage.) Advantages of using limestone include low cost, ease of use, and formation of a dense, easily handled, sludge. Disadvantages include slow reaction time, loss in efficiency of the system because of coating of the limestone particles with iron precipitates, difficulty in treating Acid Mine Drainage with a high ferrous-ferric ratio, and ineffectiveness in removing manganese. Limestone treatment is generally not effective for acidities exceeding 50 mg/l.

#### **Hydrated Lime (calcium hydroxide)**

Hydrated lime is normally the neutralizing agent of choice by the coal mining industry because it is easy and safe to use, effective, and relatively inexpensive. The major disadvantages are the voluminous sludge that is produced (when compared to limestone) and high initial costs that are incurred because of the size of the treatment plant.

#### **Soda Ash (sodium carbonate)**

Soda ash briquettes are especially effective for treating small Acid Mine Drainage flows in remote areas. Major disadvantages are higher reagent cost (relative to limestone) and poor settling properties of the sludge.

### Caustic Soda (sodium hydroxide)

Caustic soda is especially effective for treating low flows in remote locations and for treating Acid Mine Drainage having a high manganese content. Major disadvantages are its high cost, the dangers involved with handling the chemical, poor sludge properties, and freezing problems in cold weather.

### Ammonia

Anhydrous ammonia is effective in treating Acid Mine Drainage having a high ferrous iron and/or manganese content. Ammonia costs less than caustic soda and has many of the same advantages. However, ammonia is difficult and dangerous to use and can affect biological conditions downstream from the mining operation. The possible off-site impacts are toxicity to fish and other aquatic life forms, eutrophication and nitrification. Fish species generally exhibit low tolerance to unionized ammonia and toxicity levels can be affected by Ph, temperature, dissolved oxygen and other factors. A more complete review of ammonia treatment of mine drainage is given by Faulkner (1991). Ammonia use is not allowed in all States and, where permitted, additional monitoring is required.

### Constructed Wetlands

Constructed wetlands utilize soil- and water-borne microbes associated with wetland plants to remove dissolved metals from mine drainage. Initial design and construction costs may be significant, ranging into tens of thousands of dollars. Unlike chemical treatment, however, wetlands are passive systems requiring little or no continuing maintenance. This is a relatively new treatment technology with many specific mechanisms and maintenance requirements not yet fully understood. Optimum sizing and configuration criteria are still under study. Seasonal variations in metals removal efficiency have been noted with lesser amounts removed in cold weather. Wetlands are generally more effective in removing iron than manganese. The greatest utility of wetlands appears to be in the treatment of small flows of a few gallons per minute.

### **Treatment Costs**

For Acid Mine Drainage treatment Costs, OSM has developed [AMDTreat](#), a computer program to calculate long-term cost for treating mine drainage, available for download at: <http://amd.osmre.gov/>.

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