

Coal Mining and Acidic-Mine Drainage:
Causes and Abatement Techniques

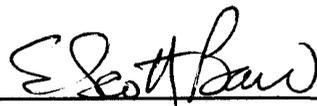
by

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A handwritten signature in cursive script, appearing to read "E. Scott Baw". The signature is written in black ink and is positioned above a horizontal line.

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ABSTRACT

The term acidic-mine drainage is applied to acidic water draining from mining areas. The chemical controls of acidic-mine drainage include the amount of mineral sulfides present in the mined rock, the crystallinity of the sulfides, and the presence of carbonate minerals. Physical controls are based on the presence of air and water. The ability of certain bacteria to catalyze the acid-producing reactions is a biological control. Acid/base accounting is an abatement technique in which the acid potential of a rock is weighed against its base potential. Various alkaline agents, primarily limestone, can be used to neutralize acidic-mine drainage. Neutralization results in an adjustment of pH and chemical precipitation. It will not decrease the iron and sulfate contents of the water. The use of phosphate rock has been proposed as an abatement alternative. It contains the mineral apatite, which has the ability to prevent the acid-producing reactions from taking place.

INTRODUCTION

Coal mining has produced the obvious benefits of increased energy supplies and opportunities for employment. However, it has also entailed costs, including adverse effects upon the environment. The most serious problem facing the coal mining industry is acidic-mine drainage. The term acidic-mine drainage is applied to acidic water draining from mining areas. The acid originates from abandoned deep mines, active deep and surface mines, refuse piles, and unreclaimed surface mines.

Coal is a sedimentary rock formed by the accumulation, alteration, and compaction of plant remains in a reducing environment like that found in a swamp. Coal sometimes contains iron disulfide minerals such as pyrite and marcasite. The acid is the product of the oxidation of these sulfide minerals.

The purpose of this paper is (1) to define and understand the chemistry of the acid-producing reaction and their chemical, physical, and biological controls, and (2) to investigate procedures for abating acidic-mine drainage.

THE FORMATION OF ACIDIC-MINE DRAINAGE

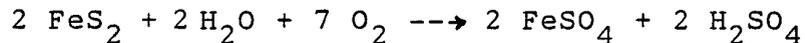
Acidic-mine drainage is a complex solution varying in quality from coal seam to coal seam, mine to mine, and even within the same mine. The production of acidic-mine drainage is dependant upon a number of variables: the amount of sulfides such as pyrite and marcasite that are present in the mined rock; the spatial distribution of these sulfides; the crystallinity of the sulfides; the size of the individual sulfide particles; and the presence of bacteria associated with acidic-mine drainage (Doyle, Bhatt, and Rapp, 1974). The presence of carbonate minerals within the sulfide aggregates also has an effect upon the rate of sulfide oxidation. The following discussion of the controls of acidic-mine drainage production is divided into three parts: chemical controls, physical controls, and biological controls.

Chemical Controls

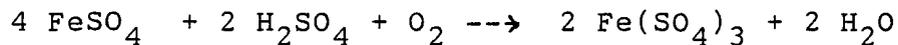
The most important chemical factors involved in the production of acidic-mine drainage are the quantity and the crystallinity of the sulfides present in the rock formation, and the presence of calcite, dolomite, or other carbonate minerals. Acidic-mine drainage results from the chemical reaction of sulfide minerals, water, and oxygen. This process is known as oxidation. The end-products of this reaction are iron sulfate and free hydrogen ions. The amount of acid produced is in part a function of the amount of sulfur contained within the rock. Organic sulfur combined with carbon does not produce acid, and usually does not make up more than one

percent of the total weight. Rocks with more than one percent sulfur by weight generally do produce acid because more of this sulfur is in the form of pyrite or other disulfide minerals (Renton, 1985). The fracturing of the rock strata and exposure of sulfide particles in particular occur as a result of the mining operation. This exposes the sulfide mineral surfaces and enables ground- and surface-water movement, allowing the formation of acidic-mine drainage to occur.

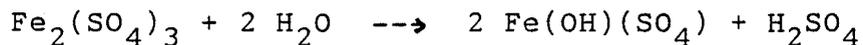
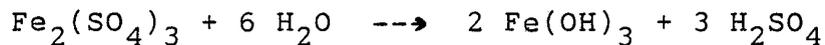
The oxidation of pyrite (FeS_2) is illustrated in the following equations:



Subsequent oxidation of ferrous sulfate (FeSO_4) produces ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$):

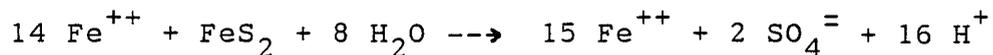


The reaction may then proceed to form a ferric hydroxide or basic ferric sulfate:



Ferric hydroxide is commonly seen as a precipitated coating on stream beds in mining areas. This is known as "yellow boy".

Pyrite oxidation also occurs due to ferric iron:



By either of these mechanisms an acidic water is produced which also is high in iron and sulfate content.

The crystalline form in which the pyrite occurs is even more important than the amount of pyrite present. Caruccio

(1977) suggests that some pyrite forms are inert, whereas "framboidal" pyrites are reactive. Therefore, a measure of framboidal pyrite, rather than total sulfur, would be a more useful indicator of acidic-mine drainage potential. Renton (1985) disagrees, pointing out that nearly all the pyrite in the low-sulfur coals of West Virginia is framboidal, and yet these coals do not produce acid. The exact chemical and structural differences among the forms of pyrite are as yet unknown, as well as why chemical reactivity is dependant upon the crystalline form of the pyrite. Both of these areas currently are being researched.

Another chemical factor involved is the carbonate content of the strata being mined. The mineral calcite, a calcium carbonate mineral which is frequently associated with coal, dissolves when in contact with water and produces an alkaline solution (Doyle, Bhatt, and Rapp, 1974). This solution reacts with the acid, creating a chemically neutral product. It is important to note that carbonate minerals do not prevent the formation of acid. They merely neutralize acid which has already been formed by the oxidation of sulfide minerals. After neutralization, the water will still have high iron and sulfate contents.

Physical Controls

The most important physical aspects of acid production are the mobile elements: air and water (Giovannitti). In the undisturbed rock layers, the sulfur-bearing minerals exist in a state of equilibrium: they are inert. It is only when

this equilibrium is upset and the sulfur becomes exposed to oxygen and water that acid is produced.

Water enters the chemical system by ground-water movement or by infiltration from the surface. The means by which water enters into the system is determined by whether the mined coal-strata is above or below the natural ground-water table. Water has two roles in the acid-producing system: it is a reactant in the oxidation of pyrite, and it provides the means by which the acid is moved from the reaction site. These oxidation reactions also can occur in any unsaturated environment in which the relative humidity approaches 100%.

Certain hydrogeologic factors control the infiltration of water. The rate of flow of water is a function of the porosity and permeability of the rock and the hydraulic gradient of the ground-water system. Bedding planes and fractures such as faults and joints within a rock also affect the rate of flow by creating zones of permeability which are higher than that in the unfractured rock. The direction of ground-water flow is a function of the geologic structure and topography of the area, as well as the location of recharge and discharge areas such as springs and streams. The rock fractures also can affect the direction of ground-water flow. These areas of high water movement are "high-risk" areas in terms of acid production and transportation of the acidic water.

Another physical factor in the production of acidic-mine drainage is temperature. The acid-producing chemical reactions take place at a faster rate at higher temperatures

(Lovell). The greatest impact of temperature is on bacterial response. The activity of bacteria which catalyze acid-producing reactions increases rapidly above 70°F and slows significantly below 40°F. Temperature also affects infiltration, as in the case of frozen ground or snow-ice cover.

Biological Controls

There also are biological factors involved in the production of acidic-mine drainage. It has been proven that certain bacteria present in mine waters speed up the rate at which the acid-producing reactions occur. The autotrophic bacteria Thiobacillus ferrooxidans have the capability of metabolizing pyrite, resulting in the formation of highly reactive sulfate ions (Lovell). These bacteria do exist and grow in environments where the acid-forming reactions take place. They do not require organic nutrients, but do require oxygen and carbon dioxide. In the natural setting, these bacteria may act as a catalyst and accelerate the oxidation reactions. The bacteria are not necessary for acid formation to occur. Without them, acid production would continue to occur, although at a slower rate.

NEUTRALIZATION of ACIDIC-MINE DRAINAGE

The term neutralization, as used in mine-drainage treatment, means adjustment of pH and chemical precipitation. Both mechanisms occur simultaneously within the chemical system. There are a number of alkaline agents which may be used to neutralize acidic-mine drainage, the most extensively utilized of these being lime and/or limestone. A list of neutralizing agents that can be used in the treatment of acid mine drainage is presented in Table 1.

The following variables should be considered in the choice of an alkaline agent (Doyle, Bhatt, and Rapp, 1974):

- (1) Cost of Agent - The least expensive agent capable of fulfilling the requirements should be used.
- (2) Availability of Agent - This is partially reflected in the cost. There may be limits on the long term availability of certain agents, particularly those made available as a byproduct of other industries.
- (3) Basicity Factor - This is defined as the grams of calcium carbonate equivalent per gram of alkaline agent. The basicity factor varies among the different alkaline agents. It is a useful tool in comparing the cost of alkaline agents. The basicity factors of some commonly used alkaline agents are given in Table 1.
- (4) Reaction Time - The rates of neutralization of the various alkaline agents vary considerably.

Table 1

NEUTRALIZING AGENTS

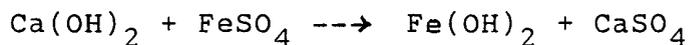
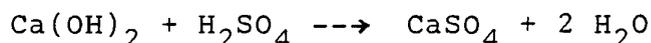
<u>Agent</u>		<u>Basicity Factor*</u>
Calcium Oxide (Quick Lime)	CaO	1.78
Calcium Hydroxide (Hydrated Lime)	Ca(OH) ₂	1.35
Calcium carbonate (Limestone)	CaCO ₃	1.00
Calcium Magnesium Carbonate (Dolomite)	(Ca-Mg)CO ₃	1.09 [±]
Magnesium Oxide	MgO	2.48
Magnesium Hydroxide	Mg(OH) ₂	1.72
Sodium Hydroxide (Caustic Soda)	NaOH	1.25
Sodium Carbonate (Soda Ash)	Na ₂ CO ₃	0.94

*Basicity Factor is defined as grams of calcium carbonate (CaCO₃) equivalent per gram of agent.

(After Doyle, Bhatt, and Rapp, 1974)

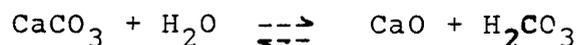
- (5) Sludge Characteristics - The settling rate and properties of the sludge are important in the design of settling tanks and in the disposal of the sludge.

Treatment with calcium alkalis is successful in that acidity is removed and the concentration of soluble iron is reduced. However, the effluent also will have a higher hardness, a higher sulfate concentration, and may contain suspended solids. The chemistry of lime neutralization is illustrated in the following equations:



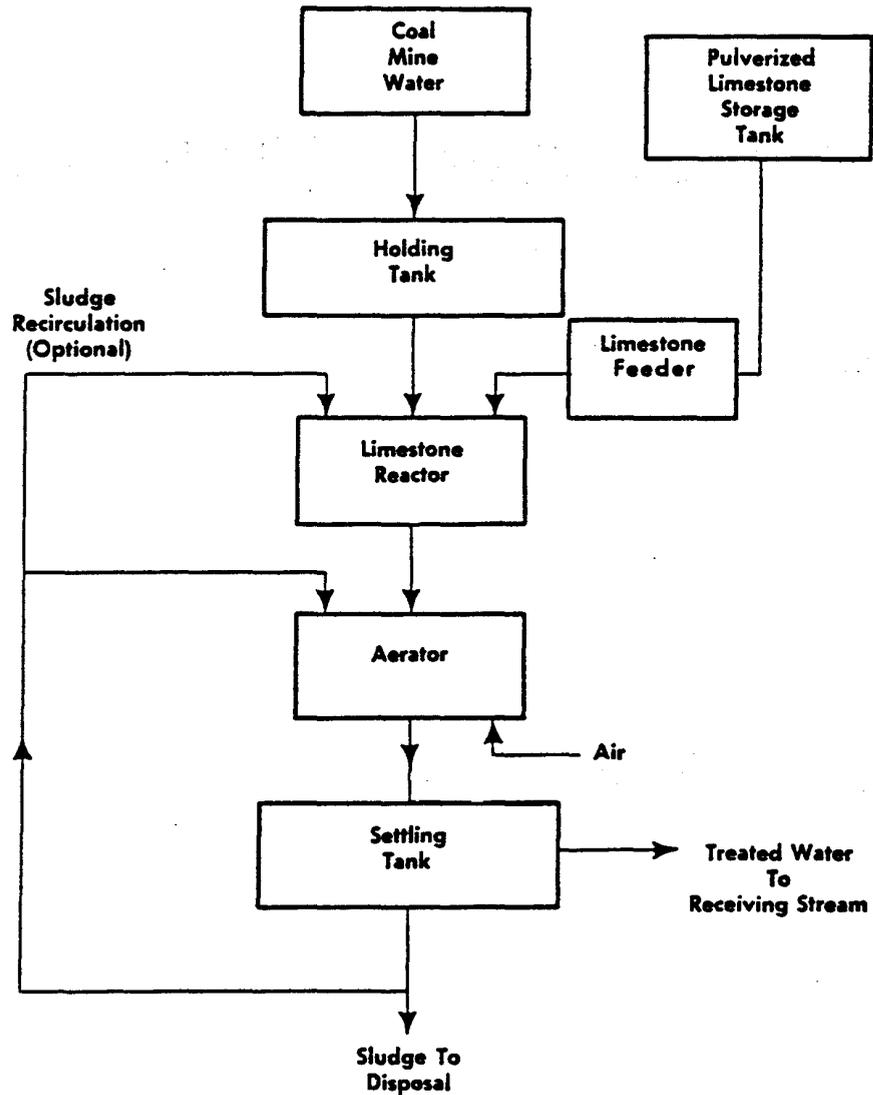
Lime treatment removes many metallic salts in addition to decreasing the acidity of acid mine drainage. Calcium sulfate (CaSO_4) will increase the pH of the water until it precipitates upon reaching its maximum solubility (Doyle, Bhatt, and Rapp, 1974).

Limestone (calcium carbonate) reacts in an acidic medium to form lime, carbon dioxide, and water:



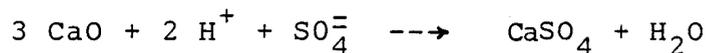
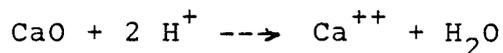
The lime reacts with the hydrogen ion of the acid to neutralize it and form water and calcium sul-

Figure 1
FLOW DIAGRAM OF A
CONCEPTUAL LIMESTONE TREATMENT PROCESS



(From Bituminous Coal Research, 1971)

fate:



Bituminous Coal Research, Inc., developed a process whereby coal mine drainage containing ferrous iron can be treated with limestone. The process results in complete neutralization of acidity and removal of iron to acceptable levels. The treatment process consists of the following operations in flow-through sequence: a) mine drainage holding, b) adding pulverized limestone and mixing, c) aerating, d) recirculation of the slurry to the mixing area, e) sludge settling and disposal. A general concept of the limestone neutralization process is shown in Figure 1.

The coal-mine drainage is conveyed to an earthen holding lagoon. It is then added to the reactor along with pulverized limestone and recirculated sludge and mixed for a period of 60 minutes. Effluent from the reactor tank flows to an aeration tank where mixing and aeration are accomplished by mechanical surface areators. The aeration tank effluent flows into the settling basin. The sludge from the settling basin is pumped from the settling basin to the sludge pump well. Recirculated sludge is pumped at a rate equal to the plant influent to the reactor tank. The remainder of the settled solids is pumped by the waste sludge pumps to earthen sludge dewatering basins for additional concentration and disposal. The supernatant from the dewatering basin is discharged to a receiving stream. A concrete pump provides the means for transfer of the

sludge to tank trucks for ultimate disposal.

To be used in the treatment process, the particle size of the limestone should be no larger than 74 microns. The limestone composition should approach pure calcium carbonate with as little magnesium content as possible. Magnesite is the least effective neutralizing agents, followed closely by dolomitic limestones (Wilmoth, 1974).

Advantages of using limestone are lower costs per unit weight, fewer safety problems handling it than more reactive reagents, and less harmful effects on the body of water receiving the effluent in case of accidental overtreatment. The use of limestone also has the advantage of a reduction in sludge volume, allowing for the use of smaller settling basins. The major disadvantage of using limestone is the long detention time required by the slow rate of oxidation of ferrous iron at the relatively low pH attainable with limestone (Bituminous Coal Research, Inc., 1971).

The use of sodium based alkalis, such as soda ash and caustic soda will effectively remove acidity and iron. However, these alkalis are significantly more expensive to use. There also is no reduction in sulfate content, due to the high solubility of sodium sulfate. The resulting insoluble materials are iron and aluminum hydroxides and oxides. The volume of these precipitants is less because sulfate is not removed from solution. Sodium based alkalis do not add to the hardness of the effluent as in the case of calcium based alkalis (Wilmoth, 1974).

EVALUATION OF THE ACID-PRODUCING POTENTIAL OF
ROCKS ENCOUNTERED IN MINING

It is known that not all coals are acid producers. Some coals can be mined without acid problems, and some coals are acid producers only in certain areas. Although acid is produced by the oxidation of sulfide minerals exposed to the atmosphere, not all exposed sulfides react. In some cases, acid-producing rocks may also be rich in calcite or other carbonate minerals. This may cause the acid to be neutralized. Therefore, if a rock contains little or no sulfides, if the sulfides are non-reactive, or if the rocks contains carbonates along with sulfides, there will be no acid problem. However, there may still be a sulfate and iron pollution problem. If a rock contains reactive sulfides but no carbonates, then it will produce acid when exposed to the atmosphere (Renton, 1985).

This problem became the basis for a research effort begun by Dr. Richard Smith, of the West Virginia University Department of Agronomy. The question was how much acid would the rocks produce, and could this potential acid production be evaluated experimentally? This research resulted in the technique of acid/base accounting to evaluate the acid producing ability of rocks encountered in mining. This method is used to predict the potential environmental impact of a proposed mine.

The two basic assumptions of acid/base accounting are:
(1) all sulfur contained in the rocks is reactive, and will produce sulfuric acid upon exposure to the atmosphere.

(2) All carbonate materials contained in the rock will dissolve to produce an alkaline solution. It also is assumed that the acid produced by sulfide oxidation will react with the alkaline solution produced by carbonate dissolution. The acidity of the resulting solution will depend upon which of the two reactions are dominant.

The first analytical procedure involved in acid/base accounting is to determine the amount of sulfur in the rock. The amount of acid that would be produced (assuming that all sulfur is reactive) is determined. The next procedure is to determine the carbonate mineral content of the rock, and the amount of alkaline solution that would be produced (assuming that all carbonates are dissolved). Whichever reaction is dominant will determine whether the overall reaction will produce an acid or an alkaline solution. The magnitude of the reaction also will be determined. If the reaction is evaluated to be acid-dominant, then it is a simple matter to determine how much carbonate material will be necessary to neutralize the excess acid. However, after the neutralization reaction takes place, the water will still contain large amounts of iron and sulfate.

Acid/base accounting has been adopted by the coal mining industry as a basis for reclamation planning. The use of acid/base accounting has resulted in significant abatement of the acid problem and increased success in surface-mine reclamation. However, the problem is not yet completely solved.

Some reclamation efforts using acid/base accounting have

not been completely successful. Systems evaluated as being alkaline have turned acidic. Other systems evaluated to be acidic and then treated with the sufficient amount of alkaline material still have turned acidic. The problem probably lies within the basic assumptions of the acid/base accounting procedure.

An example of this problem is that not all carbonate materials produce alkaline (OH^-) solutions when dissolved. Siderite (iron carbonate) will produce a neutral solution. Therefore, the acid-neutralizing potential of the rock will be overestimated. Another problem is that acid/base accounting cannot predict either the rate at which these reactions occur, or the reaction rates of the carbonates used in remediation. In a reclamation project where acidic and alkaline materials were balanced, an acidic solution may be produced if the rate of acid production is greater than the rate of dissolution of the alkaline material.

Although problems do exist with the acid/base accounting procedure, it has become the basis for all reclamation planning in West Virginia and adjoining states. Acid/base accounting was the first scientifically sound basis for reclamation planning developed (Renton, 1985).

THE USE OF PHOSPHATE ROCK AS AN AMELIORANT

To allow coal to be mined with minimal impact on the environment, it has been proposed that rock phosphate be used as an ameliorant (Renton, 1985). The mineral apatite, the major ingredient of rock phosphate, has the potential to stop the formation of acid. Apatite is the only ameliorant used or suggested thus far that has the ability to stop the acid producing reaction from taking place.

In the phosphate mining industry, there is a slurry waste product containing solids which average about 25% apatite by weight. The particles are extremely small, and are naturally maintained in suspension by clay minerals, which make up about 60% of the weight of the solids. Disposal of the waste slurries is a major environmental problem of the phosphate-fertilizer industry. Thus, the possibility exists of using the major environmental problem of one industry to solve the major environmental problem of another industry.

The phosphate ion has a strong affinity for metal ions, such as the iron ion liberated during iron disulfide oxidation. The phosphate ion reacts with metal ions to form non-polluting metal phosphates which are almost totally insoluble.

Apatite has the advantage of being soluble only under acidic conditions. Therefore, apatite would remain inactive as long as the system remains neutral or alkaline. Should the system turn acidic, the apatite would dissolve. The phosphate ion would react with the iron ion to form an insoluble phosphate. The major oxidizing agent of iron disulfide is removed from the system and

acid production would stop. As the system returned to neutrality, the apatite would cease to be soluble and would remain inert.

The phosphate slurries can be concentrated to approximately 80% solids by evaporation. The dried material can be shipped and then redispersed in water. This material then can be introduced to the reclamation system as a spray.

The slurry can be sprayed into toxic material during the construction of surface mines, or injected into fills and refuse piles. The slurry will adhere to rock due to its high clay content. It also is being investigated as a soil additive.

In these situations, the use of an alkaline agent such as limestone would not stop acid production; these materials only have the ability to neutralize acid once it has formed. The mineral apatite is the only ameliorant ever used or suggested that has the ability to stop the formation of acid.

CONCLUSION

Acidic-mine drainage is a serious environmental problem facing the coal-mining industry. There are many different controls of the production of acidic-mine drainage. These chemical, physical, and biological controls must be taken into consideration in the choice of an abatement technique.

Pre-planning allows an abatement technique to be chosen in advance. Acid/base accounting evaluates the acid producing potential of a rock strata, allowing this pre-planning to take place. Neutralization is one abatement option. Limestone or another alkaline agent is used to adjust the pH of the mine water. The use of phosphate rock has been proposed as another alternative. The mineral apatite contained in phosphate rock has the ability to keep the acid-producing reaction from taking place.

Many solutions have been proposed and tried. Current and future research appears to focus on pre-planning: finding ways to determine the acid-producing potential of a rock strata, and how to go about the abatement of acidic-mine drainage. The most promising research appears to be concentrating on a means to stop acid production from taking place, rather than simply neutralizing the acid once it has formed.

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