AT-SOURCE CONTROL OF ACID MINE DRAINAGE

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ABSTRACT

At present, there is no general solution to the problem of acid drainage from mined lands. There are, however, many options to diminish acid discharges, especially where the oxidizing pyrite is located at or near the land surface. These techniques include barrier methods that isolate the pyrite from oxygen or water, chemical additives and inhibition of iron-oxidizing bacteria. This paper emphasizes technology developed during the last decade that includes the addition of high volumes of alkalinity and/or phosphate, the use of surface geophysics to identify problem source areas, the sealing of fractured streambeds using polyurethane grout and the use of anionic surfactants to inhibit the activity of iron-oxidizing bacteria.

INTRODUCTION

Theoretically, every component of pyrite oxidation is susceptible to modification to reduce the rate of acid formation. For example, if oxygen can be excluded, as it is limited prior to mining, pyrite oxidation occurs at an insignificant rate. Similarly, if the iron-oxidizing bacteria can be eliminated, the rate of pyrite oxidation can often be dramatically reduced. Although it is easy to conceptually such steps from basic knowledge of pyrite reactivity, it is difficult to find methods that accomplish complete reaction control under field conditions. However, a partially successful control method that ameliorates contamination, either in conjunction with reclamation or independently, is preferable to the no-action alternative.

Active research on controlling pyrite oxidation can be represented by three classes of methodology. Barrier methods are those intended to
isolate pyrite from weathering reactants or from the hydrologic transport system. Chemical methods alter the composition of spoil water solutions, limit reactant availability, or serve to passivate the pyrite surface to limit oxidation. Bacterial inhibition methods represent a separate class of chemical treatment that disrupts the biologically catalyzed cyclic oxidation process. This paper will review recent work in acid mine drainage (AMD) control technology that attempts to reduce the rate of acid generation, rather than treat the acidic effluent.

**Barriers**

Reclamation. An improvement in water quality often follows regrading and revegetation of a mine site. Whatever degree of AMD control results from reclamation is probably due to physical restriction of the system. Compaction of the material reduces exposure of pyrite surfaces to oxygen and water. Covering the spoil with soil (or a soil substitute) and vegetation also increases evapotranspiration and restricts migration of water, and possibly oxygen, into the pyritic zone. Oxygen is also stripped from the pore gases by plant root and microbial respiration and by decomposition of organic mulches.

Few research reports document the effects of conventional reclamation on AMD. In several field studies, we have observed approximately 50% decreases in contaminant concentrations soon after pit backfilling. However, several small-scale studies indicate that strongly acid-producing material cannot be controlled by conventional reclamation. For example, Fugill and Sencindiver (1986) reported that initial decreases in acid loads from vegetated coal refuse lasted less than two growing seasons. Similar laboratory studies using pyritic coal refuse also showed only short-term inhibition of AMD by conventional reclamation and by compost addition [Watzlaf and Erickson, 1986].

Isolation from Water. This class of physical treatment encompasses attempts to isolate pyritic material from water as a reaction medium or as the product transport fluid. The degree of exclusion is important. Although it is possible to reduce the reaction rate, partial exclusion only restricts product transport [Kleinmann and Crerar, 1979; Geidel, 1980; Watzlaf and Hammack, 1989]. The build-up of soluble iron sulfate salts that continues as long as even a modest amount of moisture is present, represents a reservoir of acidity that adversely affects ground water quality when the material does encounter infiltrating water, such as during spring thaw or major storm events. Annual acid load may be reduced, but occasional slugs of high acidity can be extremely detrimental to downstream activity. To attain this reduction in total acid load, compacted earth materials and synthetic liners have been used as physical barriers. Alternatively, surface diversions have been used to limit runon flow. French drains and regrading to a sloped surface have also been used to decrease the amount of contact between water and pyrite. Conventional reclamation is separated from this class of options since its chief purpose is to support revegetation, although evapotranspiration can be considered to limit water.

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Selective placement of pyritic material is commonly used as a barrier method to acid production. High and dry placement in the backfill is intended to isolate pyrite from the oxygenated, moist surface zone and from intermittent saturation. Selected non-reactive horizons are kept isolated during mining for strategic backfill construction. The most widely known plan of this type, published by the West Virginia Surface Mine Drainage Task Force [1979], includes placement of porous, non-reactive spoil at the spoil/rock interfaces and burial of pods of pyritic material above the water table but as deep as the porous base pad permits. Compaction of the spoil or application of a clay or soil cap above the pyritic material is intended to further reduce pyrite/water contact.

Applications of this method have received mixed reviews in practice from industry. The important question is whether the theories are basically sound and implementation faulty, or the reverse. Too few controlled studies have been published to settle the argument. It must be remembered that the field applications labeled as unsuccessful selective handling trials may indeed have reduced the rates of pyrite oxidation or product transport. The criterion for success, namely compliance with discharge water quality standards, may simply be too stringent. A 50% reduction in contaminant levels for non-active sites is still of value, particularly in applications where untreated water discharges directly into surface streams.

Selective placement is unsuitable for use where virtually all of the waste has a high acid potential. In such cases, capping the pyritic material with low-permeability material could reduce contact between water and pyrite. A compacted clay cap, in addition to the WV Task Force plan, was used at a surface mine in West Virginia [Geidel and Caruccio, 1985]. Although those authors believed that the clay seal effectively isolated the underlying spoil, a tracer placed beneath the clay was detected in intermittent spikes in discharge samples. Seep acidity levels were in the range of 500 to 1,500 mg/L as CaCO₃ in the second year following reclamaton. Water quality continued to deteriorate afterwards.

A more exotic cover material application was made to control acid drainage at a site in West Virginia [Caruccio, 1983]. A portion of the site was covered with 20-mil-thick plastic sheeting between October 1981 (40% covered) and June 1982 (100% covered). Two seeps had previously been identified as primary surface discharges for the covered area. A five- to tenfold reduction in acid loads was observed following partial coverage, and a further two- to sixfold reduction occurred about 6 months after complete coverage. Only small decreases in acid load were observed over the same time period in seeps draining other portions of the site [Caruccio, 1983]. However, the high cost of synthetic covers probably preclude their use at all but the most acidic sites.

Excluding water from underground mines is generally based on reducing inflow by the sealing of fractures in surface water channels or surrounding rock strata, or by the lowering of the piezometric surface by the pumping of non-acidic ground water.

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The general source of inflow water are fractures in the strata overlying the underground operations [Hobbs, 1981; Hollyday and McKenzie, 1973; Williams et al., 1986]. Streams intercepted by such fractures are often the largest single component of mine inflow and associated AMD. Multiple infiltration zones (both natural and induced) usually exist, which can cause partial to total loss of streamflow. The extent of streambed damage is controlled by such factors as depth of cover, stream orientation and geological conditions.

In two studies, electromagnetic terrain conductivity surveys performed within stream channels successfully identified water-saturated zones, presumably associated with fractures, at relatively shallow depths between 10 and 50 ft (3 and 15 m). Zones of increased conductivity were found to be positively associated with areas exhibiting significant loss of flow. Conversely, zones which exhibited reduced conductivity delineated areas where flow losses were not present. Using this information, an experimental grouting procedure was used to inject expandable polyurethane grout a few feet (less than a meter) beneath the streambeds across the loss zone. The grouting efforts resulted in 95-100% flow recovery for streams overlying an abandoned room-and-pillar mine and an active longwall operation [Ackman et al., 1989].

The conductivity surveys represent a significant time and cost savings when compared to conventional full-year gaging work typically necessary for delineation of stream loss zones. Conductivity data also resulted in the accurate prediction of a loss zone prior to longwall mining at one site.

The new stream-sealing technique was demonstrated to be quick and easy, causing minimal disturbance to the natural conditions. The shallow grouting approach appears to be more effective and much less expensive than conventional stream sealing methodology (clay-lining with rock riprap or using synthetic liners) [Ackman et al., 1989]. Although one of the principal objectives of this technology was reduced acid generation, no attempt was made to determine what effect, if any, there was on water quality as a result of reducing mine water inflow, since it was impossible to isolate and monitor the affected mine area.

Similarly, although there are many examples of alternative approaches used to exclude water from underground mines, most were undertaken to enhance worker safety or mine productivity. Wahler and Associates [1979] reported on a pilot-scale dewatering well project undertaken to reduce AMD treatment costs at an underground mine in western Pennsylvania. Although mine water inflow was reduced (well-effectiveness was projected to range from 50 to 80%), the approach was not cost-effective at that site compared to simply pumping and treating AMD. The authors concluded that the use of angled drain holes drilled from within the mine would have been more economical. A similar well-dewatering study [Schmidt, 1985] was undertaken at a site in northern West Virginia, but due to variations in mine water inflow that were probably unrelated to the dewatering effort, effectiveness in controlling AMD could not be determined.
In general, it appears that mine water inflow can be significantly reduced or excluded by dewatering and/or grouting, but that it cannot generally be justified solely on the basis of AMD treatment costs. Other aspects, such as enhanced worker safety, mine productivity, and surface water protection must be considered along with reduced AMD treatment to justify the expense of such efforts.

**Isolation from Oxygen.** Oxygen is required for direct oxidation of pyrite, for ferrous-to-ferric iron cycling, and for respiration of the iron-oxidizing bacteria. Early laboratory studies [Braley, 1960; Clark, 1965; Morth and Smith, 1966; Rogowski and Pionke, 1984; Nicholson, Gillham and Reardon, 1988] showed that the rate of pyrite oxidation was dependent on the partial pressure of oxygen. However, there was no general consensus among researchers: reaction orders of 1/2, 2/3, 0.81, and 1 were proposed [Nicholson, Gillham and Reardon, 1988; Lowson, 1988].

Recent research examined pyrite oxidation on three different scales: (1) pyrite surfaces to a depth of 20 angstroms; (2) 5-g quantities of pyrite in small columns; and (3) 175-kg quantities of pyritic shale in large columns [Hammack and Watzlaf, 1990].

Results of micro-scale studies indicated that abiotic oxidation of fresh pyrite surfaces was independent of oxygen partial pressures above 10% (0-order reaction) and was proportional to oxygen partial pressures below 10% (first-order reaction). However, the rates of abiotic oxidation measured in small columns were proportional (first order) to oxygen partial pressures between 21% (atmospheric) and 5%. Small-column and large-column results indicated that with iron-oxidizing bacteria present, the rate of pyrite oxidation was independent of oxygen partial pressures down to 1% (figure 1). Below 1% oxygen, the reaction rate was proportional to oxygen partial pressures (first-order reaction). The oxygen-impermeable and oxygen-consumptive barriers other than water that are economically feasible at present are not capable of maintaining oxygen levels below 1%.

![Figure 1. Rates of pyrite oxidation at different oxygen partial pressures.](image-url)
Therefore, no reduction in the rate of pyrite oxidation would be realized using these techniques unless the iron-oxidizing bacteria were inhibited. These experiments also indicate that bacterial inhibition is only effective only if oxygen concentrations are already low enough to limit the rate of abiotic oxidation. Otherwise, the best method for limiting pyrite oxidation is to place the pyritic material below a permanent water table.

Complete reaction of the oxygen in oxygen-saturated water (mg/L D.O.) can produce only about 5 mg/L of iron and 17 mg/L of sulfate from pyrite. Oxygen replenishment, involving gas-to-liquid mass transfer, is a slow process and thought not to be important. For example, in the large-column experiments just discussed, a 96% reduction in pyrite oxidation was realized by inundation [Hammack and Watzlaf, 1990]. It needs to be emphasized, however, that inundation must be complete and constant to be effective. The dip of strata sometimes makes this very difficult.

Techniques that isolate pyrite from water also can limit oxygen, but do not typically reduce oxygen sufficiently to reduce the bacterially-catalyzed reaction system. A possible exception is a new approach, still being evaluated, in which already-buried, acid-producing material is located using magnetometry and selectively grouted with a pozzolanic mixture of cement and fly ash [Ackman, 1990].

Chemical Methods

Chemical methods are intended to disrupt the AMD system in various ways. It is easier to classify these methods by the nature of the treatment chemical than by the mode of action.

Alkaline Addition. The most widely-used abatement chemicals are alkaline compounds such as sodium hydroxide (NaOH, lye, caustic soda), limestone (CaCO₃, agricultural lime), lime (CaO-quick lime, Ca(OH)₂-hydrated lime), and sodium carbonate (Na₂CO₃, soda ash). Neutralizers are more often used for after-the-fact water treatment. However, there is significant evidence that addition of alkaline material can produce an environment unfavorable to pyrite oxidation. First, the iron-oxidizing bacteria require an acidic environment for optimum activity. Second, near-neutral pH causes ferric iron to precipitate, with possible effects including coating of reactive pyrite surfaces and disruption of the ferric oxidation pathway. Both laboratory and field studies support lower AMD production rates at high pH [Kleinmann et al., 1981; Nicholson et al., 1988].

Many application methods are available. A key feature of successful application is to load the water with alkalinity prior to contact with pyrite. At surface mines, alkaline solids can be placed on the pavement, layered in the backfill, or admixed with spoil. Heavy surface covers of limestone, initially used to facilitate revegetation, also can inhibit AMD formation [Geidel and Caruccio, 1984; Waddel et al., 1986]. Although the effectiveness of this approach appears to be limited to sites where acid potential does not greatly exceed the natural alkalinity, others have attempted to
enhance the effectiveness of alkalinity by placing a mixture of limestone and sodium carbonate in areas of induced alkaline recharge, again with some beneficial effects [Caruccio and Geidel, 1984; Caruccio and Geidel, 1986].

There have been several attempts to add alkaline compounds through boreholes to mine spoil and/or to the perched water table at abandoned and inactive mines. Most of the attempts have used a lime/water slurry and have been unsuccessful since most of the lime is only suspended, due to limited solubility, and apparently falls out of suspension relatively close to the injection site [Ladwig et al., 1985]. Injection of more soluble chemicals (i.e., sodium carbonate and sodium hydroxide) obviates this problem, allowing for in-place neutralization of the mine water, but has not been shown to actually limit acid production. This is reasonable since the alkaline material is either injected into the saturated zone, or rapidly percolates down to that zone, allowing for little interaction between the alkaline fluid and the reactive pyrite in the unsaturated zone. Thus, it would appear that alkaline injection into surface mine spoil material only serves as an alternative to conventional water treatment, requiring lower initial capital investment and only periodic appearances at the site. A field test now being conducted at a partially-flooded, abandoned underground mine by the U.S. Bureau of Mines, should help to determine the practicality of such an approach.

Phosphate. The addition of phosphate to acid spoil has been proposed as a method to slow the rate of pyrite oxidation. The presumed mechanism of action is the formation of relatively insoluble iron phosphates \((\text{Fe}_3(\text{PO}_4)_2 \text{ and FePO}_4)\), lowering the concentration of ferric iron available for reaction with pyrite. A patent was issued in 1969 for a method to control acidity produced from pyrite and other sulfur compounds by adding inorganic phosphate [Flyn, 1969]. Little notice was given to the concept for mining applications until the 1980s. Laboratory studies [Meek, 1984; Stiller et al., 1986] showed that the addition of crushed apatite rock \((\text{Ca}_3(\text{OH})(\text{PO}_4)_2)\) reduced acid production by as much as 96% at doses less than 3 ppt (3 tons/1,000 tons). A subsequent field experiment [Stiller et al., 1986] indicated that phosphate addition at 3 ppt slowed acid production from shale/coal for about one year following construction of the model fills, but that inhibitory effect appeared to diminish somewhat through the second year. Subsequent laboratory work indicated that a minimum effective application rate is about 1 weight % apatite, and that in the laboratory, acid generation can be reduced up to 90% at application rates of 4-5 weight % apatite [Renton et al., 1988]. Field tests with 4,000-ton and 100,000-ton piles of coal refuse are now being initiated using application rates of 0-4% commercial rock phosphate added per ton of coal refuse [Ziemkiewicz, 1990].

Bacteria Inhibitors

Iron-oxidizing bacteria often control the rate of pyrite oxidation once the system is in a highly acidic state. Of the many classes of compounds identified by microbiological studies to inhibit the iron-oxidizing \(\text{Thiobacillus ferrooxidans}\), only anionic surfactants have
proven to be effective in the field [Kleinmann et al., 1981; Kleinmann and Erickson, 1983].

Initial laboratory studies showed that anionic surfactants such as sodium lauryl sulfate (SLS) and alkylbenzene sulfonate (ABS) reduced pyrite oxidation in simulations of AMD-forming environments. The inhibitors were as effective as sterilization at dosages on the order of 25 to 50 mg/L [Kleinmann and Crerar, 1979]. Subsequent studies showed that surfactants applied in solution adsorbed to coal refuse and spoil, so that the active agent did not wash through the oxidizing zone immediately [Kleinmann and Erickson, 1983].

Several full-scale field trials of surfactant application were conducted by the BOM. The first full-scale field test, an 11-acre, acid-producing coal refuse pile, was sprayed with 550 gallons of 30% SLS diluted with local stream water. Following a 3-month lag time, acidity and sulfate concentrations dropped by about 60% and iron concentrations decreased by 90%. The single treatment was effective for approximately 6 months, until the surfactant washed out or degraded to less than inhibitory concentrations [Kleinmann and Erickson, 1983]. In a similar application at an active refuse disposal area, SLS treatment reduced contaminant levels by about 90% for 3 three months. Not all field trials have been successful, however. For example, detergent applications to acidic spoil overburden has generally not been effective, presumably because oxygen concentrations at depth are adequate to sustain a high level of abiotic pyrite oxidation.

Incorporation of the active agent in an elastomeric matrix allows controlled release by diffusion of the surfactant to the elastomer surface, followed by dissolution during contact with moisture. Commercial ABS controlled-release pellets, with release lifetimes of 2 to 7 years, have been developed, and were field tested in conjunction with a single application of liquid surfactant [Kleinmann, 1982; Sobek et al., 1985; Sobek et al., 1990]. Use of this approach significantly improves drainage quality and revegetation, and appears to have residual effect even after bactericidal release has finished [Sobek et al., 1990].

Several other inhibitors have been tested in the laboratory for AMD-control applications. Sorbate and benzoate salts, commonly used in food preservation, were shown to inhibit T. ferrooxidans and AMD production from coal refuse in pilot-scale tests [Erickson et al., 1985; Onysko, 1986]. At equivalent concentrations, benzoate and SLS tended to exert slightly stronger inhibition than sorbate. More recently, nitrapyrine, commercially used to control the activity of nitrifying bacteria, has been shown in the laboratory to effectively inhibit T. ferrooxidans at concentrations low enough to indicate that it may serve as an inexpensive alternative to anionic surfactants [Sherrard et al., 1990].

SUMMARY AND CONCLUSIONS

At present, there is no general solution to the problem of acid drainage from mined lands. There are many options, each of which may
At present, there is no general solution to the problem of acid drainage from mined lands. There are many options, each of which may diminish acid discharges, but there are very few cases where acid generation can be completely controlled. The number of options available continues to increase, however, as mining companies and researchers develop and evaluate new alternatives to long-term water treatment. At-surface sources of acid drainage are most amenable, at present, to control due to their accessibility and due to the fact that researchers have found it easier and less expensive to conduct their experiments at such sites. Researchers in the future need to focus more on the control of acid generation at underground sites, both active and inactive, for these sites produce proportionally, much greater AMD, and continue to do so for much longer periods of time.

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