

TREATMENT OPTIONS FOR ACID MINE DRAINAGE

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INTRODUCTION

The basis of acid mine drainage (AMD) production is fairly well understood (Kleinmann et al., 1981; Nordstrom, 1982; and Onysko, 1986). Pyrite and other sulfide minerals, on exposure to oxygen and water, oxidize to produce dissolved metals, sulfate, and acidity. The process is catalyzed by iron-oxidizing bacteria, such as *Thiobacillus ferrooxidans*. The resulting solution interacts with other mine waste constituents in secondary reactions such as neutralization, ion-exchange, and acid-induced metal dissolution. Consequently, the discharge water quality can range from the classic acid mine drainage (AMD) formula of high acidity, metals, and sulfate concentrations to a neutralized version of low metal and high sulfate content. Acid discharges often persist at unreclaimed sites for many decades; some can be considered a perpetual pollution source.

At most active mine sites where AMD is a problem, the water is pumped to a central location to be mixed with an alkaline chemical, such as lime or sodium hydroxide, and mechanically aerated in large basins. Sufficient alkalinity is added to raise the pH to between 6 and 9, which causes most metals to hydrolyze and precipitate as a sludge. Some metals, such as iron, must be oxidized to be precipitated as a stable compound, which is why aeration is often required. The resultant sludge-water mixture then flows to a clarifier or a series of settling ponds. Enormous volumes of sludge, 5 to 10% of the total AMD flow, are produced. A study of 33 AMD treatment plants in western Pennsylvania found an average treatment plant flow for these facilities to be over 26,000 m³/d (0.31 m³/s) (T. Ackman, 1982). At 10% of the flow, over 1 Mm³ of sludge was being produced annually from this small sampling of AMD treatment facilities.

The overall cost of AMD treatment to the U.S. coal mining industry exceeds \$1

million a day! A major focus of the Bureau of Mines' AMD research program is to reduce these water treatment costs. This paper will present some of the results of this research.

IN-LINE AERATION AND NEUTRALIZATION

Where appropriate, one way to reduce costs is to use an in-line aeration and neutralization system (ILS) instead of a mechanical aerator and mixing basin. The ILS consists of two commercially available components, a jet pump (ejector) and a static mixer (Ackman and Place, 1987). The jet pump is simply a nozzle that converts water, already under pressure, into a high-velocity stream that entrains air by Venturi action.

A jet pump used to treat acidic mine water should be made of polyvinyl chloride (PVC) to avoid corrosion problems and to more easily address any build-up of calcium sulfate (gypsum). Water enters under pressure and is converted by the jet pump into a high-velocity stream, which passes through a suction chamber that is open to the atmosphere. If the system is being used for neutralization, as well as aeration, the suction chamber also serves as the injection point for the alkaline material. Multiple jet pump units may be placed in parallel as long as water pressures of at least 20 psi (138 k Pa) per jet pump are maintained. A water pressure of 50 psi (345 K Pa) is considered optimal.

After passing through the jet pump, the flow of air and liquid enters the static mixer to aid oxygen dissolution. There are various types of static mixers. One design, used extensively in the field, consists of eight 1 ft (0.3 m) sections of

pipe made of copolymer polypropylene resins, laminated with fiberglass. Inside each section is a helical element that forces the water to follow a spiral path. Each section is rotationally offset 90° from its neighbor to enhance the mixing action. Figure 1 depicts an actual ILS set-up at a mine site. The ILS unit shown is portable and can treat, at most, about 500 gpm. Larger ILS units have been constructed to treat flows up to 2800 gpm.

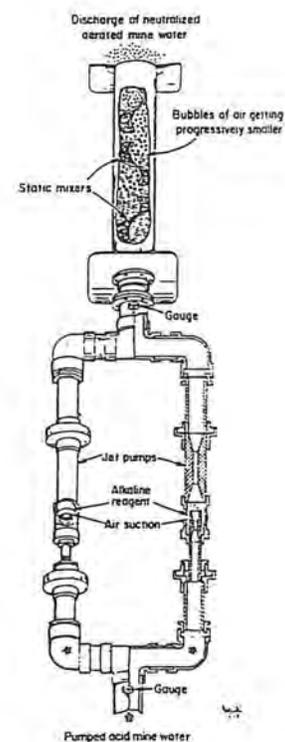


Figure 1.--A schematic of the In-Line System (ILS), used to aerate and neutralize AMD.

An alternative static mixer design, and the one recommended for most

applications, consists of vertical airlift aeration units that contain trickling media (hollow plastic cylinders with internal baffles). These media are used routinely in sewage and industrial waste treatment and increase the mixing capacity and oxygen transfer of the ILS by enhancing bubble shear and by extending the air-water contact time.

The ILS has proven to be effective in treating acidic mine water at a number of sites. The influent water quality of some of the sites successfully treated with the portable ILS unit are shown in Table I. In general, a pH of 6.9 - 7.7 lowered iron concentrations of up to 300 mg/L to less than 3 mg/L (the typical U.S. coal mine effluent limit). At site 8, a second pass through the ILS was necessary to meet effluent requirements due to the limitations of the portable system. At two sites (1 and 2), neutralization costs for the ILS could be compared with the costs of conventional treatment. Site characteristics for these two sites are shown in Table II.

At the first site, where lime was being used, the mine water was pumped into an existing basin, then pumped through the ILS and discharged via a flume into a large clarifier. A diesel-powered, submersible pump operated the 3-jet ILS used at this site. Neutralization consisted of pumping a lime slurry from a mix tank into the suction chamber of one jet pump. An average of 91% of the Fe^{2+} and 68% of the Mn was removed at pH 7. At pH 7.7, 98% of the Fe^{2+} was removed; at pH 8.4, over 99% of the Fe^{2+} was removed. Effluent manganese concentrations were less than the legal limit of 2 mg/L at pH 7.7 and above.

At Site 2, water was pumped from a raw water pond, through a 2-jet configuration of the ILS, and discharged into a sludge settling pond. NaOH was injected into one jet with a metering pump. With one exception, Fe^{2+} concentrations were reduced to less than 1 mg/L at pH values of 7.2 and up, regardless of operating pressure. Effluent Mn concentrations were found to be above effluent limits until the pH was raised to 9.1.

In a conventional AMD treatment facility, lime is slurried with water and then mixed with the mine water. In practice, this means that a great deal of lime falls to the bottom of the aeration tank and is wasted. At site 1, the ILS proved to be 30% more efficient than the normal plant requirements, based on actual lime used. Based on analysis of the neutralized water and sludge, it appears that this enhanced efficiency is due to the superior mixing action of the ILS.

At Site 2, the average rate of NaOH use in the existing plant for a 6 month period was determined from company records. When compared to the NaOH feed rates required with the ILS to meet effluent standards, a 29% reduction in NaOH use was observed. The ILS feed rates were measured in the field and confirmed by chemical analysis. At this site, it appears that the enhanced efficiency of the ILS was due to the superior oxygen transfer capability of the ILS, which allowed contaminant removal at a lower pH than was possible with the existing treatment plant.

At relatively low contaminant concentrations, the oxidation rate for iron and manganese increases with

Table I.--Influent water qualities effectively treated to within effluent standards.

| Parameter | Field Sites | | | | | | | | Effluent Standards | |
|-------------|-------------|-----|-----|-----|------|-----|------|------|--------------------|-----------|
| | 1* | 2* | 3 | 4 | 5 | 6 | 7 | 8 | Daily max | Mthly avg |
| pH | 5.3 | 2.9 | 2.9 | 4.5 | 6.7 | 3.7 | 3.1 | 2.8 | between 6 and 9 | |
| Net acidity | 991 | 736 | 808 | 810 | -222 | 510 | 382 | 3772 | N/A | N/A |
| Ferrous Fe | 527 | 82 | 77 | 190 | 15.6 | | | 965 | N/A | N/A |
| Total Fe | 529 | 145 | 150 | 260 | 20.2 | | 23 | 1011 | 6.0 | 2.0 |
| Mn | 14.1 | 121 | 9.6 | 0 | 0 | 181 | 20.4 | 68.4 | 4.0 | 2.0 |

*Field sites discussed in this paper

Table II.--Conventional treatment at Sites 1 and 2.

| <u>Site Description</u> | <u>Site 1</u> | <u>Site 2</u> |
|-------------------------|---------------------------------|--------------------|
| Operation | Abandoned underground coal mine | Surface coal mine |
| Raw water | Mine pool | Pond |
| Sludge settling | Clarifier | Pond |
| Aeration | Mechanical | None |
| Neutralization | Ca(OH) ₂ (lime) | NaOH |
| Normal flow | 1500 gpm (95 L/s) | 220 gpm (13.9 L/s) |

increasing pH. It is therefore common practice to raise the pH to 10 or greater to achieve adequate floc formation and to precipitate manganese. However, for most AMD, improving the aeration and mixing processes is more effective and much less expensive. Additional information on the importance of oxygen transfer and how to calculate the aeration requirements of an ILS system is available (Hustwit et al., 1992).

WATER TREATMENT UNDERGROUND

The portability of the ILS makes it possible to treat mine water underground, to further reduce water treatment costs. Two conceptualized approaches to prevent acid mine pools are based on underground water treatment. In one case, the treated water and sludge are co-disposed within an abandoned, hydrologically isolated section of the underground workings to

create an alkaline mine pool that will (1) exclude oxygen and limit future acid production, (2) neutralize or buffer residual acid production from unflooded levels, and (3) serve as a sludge disposal site. As the section becomes inundated, good quality water will be allowed to pass through pressure release mechanisms (pipes with valves) placed in the bulkheads, and will be discharged to the surface (Figure 1). In the other case, only the treated water containing excess alkalinity is discharged in the same manner as case 1; i.e., into an abandoned, hydrologically isolated section to neutralize an existing, acidic pool. The sludge is sequestered from the treated discharge and processed through a two stage sludge dewatering operation. This operation allows the sludge to be stored for later disposal into an alkaline area or to be incorporated into bulkhead construction.

A related practice is currently underway at an underground mine site in northern Virginia. The Powell Mountain Coal Company, which is in the early stages of the operation, has initiated the practice of inundating a mined out section to avoid future acidic drainage and post-mining water treatment. NaOH is being added to the developing pool of water to maintain alkaline conditions.

In addition to creating an alkaline mine pool underground, treating the water in the mine should also simplify the issue of dealing with the AMD sludge. Since the mine water never left the mine, one doesn't have to obtain a class 5 injection well permit from the Environmental Protection Agency to dispose of it underground. Since sludge disposal is a major cost at many

operations, this aspect alone may justify a decision to try this approach.

PASSIVE MINE WATER TREATMENT

The passive treatment of contaminated coal mine drainage is a rapidly growing and evolving technology. Passive systems typically require less operation and fewer maintenance efforts and are less expensive than conventional treatment systems. As a result, over 500 passive systems have been constructed in the U.S. to treat AMD. Three principal types of passive technologies currently exist for the treatment of coal mine drainage: the aerobic system, the compost wetland, and the anoxic limestone drain.

In aerobic systems, oxidation reactions occur and metals precipitate as oxides and hydroxides. Most aerobic systems are simple wetlands; they contain cattails growing in a clay or soil substrate. Aerobic systems are designed to facilitate oxidation and precipitation of iron and manganese by bacterial catalysis and abiotic reactions. Many aerobic systems have been constructed at sites where the mine water naturally contains sufficient alkalinity to buffer the acidity generated by the metal hydrolysis reactions. In these systems, the removal of iron is limited by dissolved oxygen concentrations and detention time. The detention time is related to the size of the system and the flow rate, which allows one to calculate a minimum size for the system based on the load of iron that has to be removed daily. For water which is net alkaline, experience has shown that

$$\text{Minimum wetland size (m}^2\text{)} = \frac{\text{Fe loading (g/day)}}{20} \quad (1)$$

Manganese removal only occurs in aerobic systems where the pH is 6 or above, and generally occurs only after iron oxidation is complete, which requires that additional area be set aside at sites where manganese is a problem.

$$\text{Additional wetland area (m}^2\text{)} = \frac{\text{Mn loading (g/day)}}{5} \quad (2)$$

When building an aerobic wetland, always keep in mind the goals of the system: to aerate the water and to retain the water long enough for oxidation and precipitation reactions to occur. A typical aerobic wetland is constructed by planting cattail rhizomes obtained on- or near-site in soil or alkaline spoil. Some systems have been planted by simply spreading cattail seed heads, with good plant growth attained after 2 years. The depth of the water in a typical aerobic system is 6-18 inches. Often, several wetland cells are connected by flow through a V-notch weir, railroad tie steps, or down a ditch.

Plants do not appear to be essential in passive treatment of alkaline mine water. Several systems have been constructed that have little emergent plant growth. Flow is through open water ditches or ponds. In one case, where Mn is targeted for removal, water flows through a pond filled with limestone rocks. Removal of metals in these plantless, aerobic systems appears to occur at rates similar to alkaline aerobic systems containing plants (Hedin and Nairn, 1992).

However, we still recommend that plants be included because they help filter particulates, prevent flow channelization and provide wildlife benefits that are valued by regulatory and environmental groups.

At sites where acidity exceeds alkalinity, two techniques have been used to increase the pH: wetlands constructed with composted organic material and anoxic limestone drains. Compost wetlands are similar to aerobic wetlands in form, but also contain a thick organic substrate. This substrate promotes chemical and microbial processes that generate alkalinity and neutralize acidic components of mine drainage. Typical substrates used in these wetlands include spent mushroom compost, peat moss, haybales, and manure. The term "compost wetland" is general and is meant to include any wetland which contains an organic substrate in which biological alkalinity-generating processes occur.

An alternative method for passively treating AMD is to pretreat the water with limestone and transform it into alkaline mine drainage. Such systems, called anoxic limestone drains (ALD), have been constructed at sites in northern and southern Appalachia (Turner and McCoy, 1990; Brodie et al., 1990; Nairn et al., 1991). The systems function by causing the acidic mine water to flow through a limestone bed before it surfaces. In the anoxic environment that generally exists within the buried limestone bed, iron oxidation reactions do not occur and the limestone does not armor with ferric hydroxides. Instead, limestone dissolution occurs and the water is charged with bicarbonate alkalinity. Because limestone is

extremely inexpensive, it has often been cost-effective to include enough limestone in anoxic limestone drains to theoretically last decades.

An ALD can produce alkalinity at a lower cost than can compost wetlands. However, not all water is suitable for pretreatment with an ALD. The primary chemical factors believed to limit the use of an ALD are the presence of Fe^{3+} , dissolved aluminum (Al) and dissolved oxygen (DO). When acidic water containing any Fe^{3+} or Al contacts limestone, both metals hydrolyze and precipitate. No oxidation is necessary. Ferric hydroxide can armor limestone, limiting its further dissolution. Whether aluminum hydroxides armor limestone has not been determined. The buildup of both precipitates within the ALD may eventually decrease the drain permeability and cause plugging. The presence of any DO in mine water will promote the oxidation of ferrous iron to ferric iron within the drain, and thus potentially cause armoring and plugging. While the short-term performance of an ALD that receives water containing elevated levels of Fe^{3+} , Al or DO can be spectacular (total removal of the metals), the long-term performance and longevity of these systems is questionable.

Although some mine waters appear to be ideal for pretreatment with an ALD, the use of an ALD for other waters will most likely result in failure in a relatively short time. For example, one ALD constructed with size 2B limestone received mine water containing 25 mg/L Al. Flow through the ALD was compromised in less than a year of operation. The mine water began to seep through the clay spoil material behind the ALD rather than flowing

through the limestone gravel. The use of larger #3 and #4 limestone may have allowed the precipitates to pass through the ALD.

To whatever extent mine water contains DO, Fe^{3+} , or Al, the effective lifetime of an ALD will probably be compromised in some way. The limiting concentrations or loads of these parameters are unknown at the present time, but given the current understanding of both ALDs and compost wetlands, the following criteria are suggested for determining the most cost-effective method for treating acidic water passively.

When DO, Fe^{3+} and Al are acceptable for an ALD

Mine water with low levels of DO, Fe^{3+} and Al is currently considered to be suitable for pretreatment with an anoxic limestone drain. Mine water intercepted after it contacts the atmosphere usually will not fulfill these criteria. In an ALD, alkalinity is produced when the acidic water contacts the limestone. It is considered important to use limestone with a high CaCO_3 content because of its higher reactivity compared to a limestone with a high MgCO_3 or $\text{CaMg}(\text{CO}_3)_2$ content. Most effective systems have used #3 or #4 (baseball size) limestone. Some systems constructed with limestone powder and gravel have failed, apparently because of plugging problems. The ALD must be sealed so that inputs of atmospheric oxygen are minimized and the accumulation of carbon dioxide within the drain is maximized. This is usually accomplished by burying the ALD under several feet of clay. Plastic is commonly placed between the limestone and clay

as an additional gas barrier. In some cases, the ALD has been completely wrapped in plastic before burial (Skousen and Faulkner, 1992). The ALD should be designed so that the limestone is inundated with water at all times. This has been accomplished with clay dikes within the drain or riser pipes at the outflow of the drain.

The design of ALDs has varied. Most older ALDs were constructed as long narrow drains, approximately 2-3 feet wide. At sites where linear drains were not possible, anoxic limestone beds have been constructed that are wider (30-50 feet). The bed systems have produced alkalinity in concentrations similar to the drain systems.

The proper sizing of ALDs is uncertain. Theoretical calculations can be performed to estimate the mass of limestone required to neutralize a certain discharge for a specified period of time. Important to these calculations is the alkalinity concentration expected to be produced by ALDs. A maximum value of approximately 300 mg/L has been observed at ALDs constructed recently. The minimum mass of limestone needed to treat a year's flow of mine water can be calculated from the flow rate and an assumption that the drain will produce 300 mg/L alkalinity.

$$\text{yearly CaCO}_3 = \text{flow (Lpm)} \times 158 \quad (3)$$

consumption
(kg)

or, where flows are measured in gallons and masses are calculated in tons:

$$\text{yearly CaCO}_3 = \text{flow (gpm)} \quad (4)$$

consumption $\times 0.6565$
(tons)

Limestone used in ALDs has a density of about 1.0-1.5 ton/yd³.

In order to determine the total mass of limestone needed in the drain, the above calculation must be adjusted for the CaCO₃ content of the limestone and the projected lifetime of the ALD.

When these calculations are done properly and carried through into the actual construction of the ALD, they assure that there is theoretically enough limestone in the drain to generate alkalinity for the time period considered. Because the oldest ALD installations are only 3-4 years old, it is difficult to assess how realistic these theoretical calculations are. Questions about the ability of drains to maintain unchannelized flow for a prolonged period of time, whether 100% of the CaCO₃ content of the limestone can be expected to dissolve, whether the drains will collapse after significant dissolution of the limestone, and whether inputs of DO that are not generally measured with standard field equipment (0-1 mg/L) might result in armoring of the limestone with ferric hydroxides, have not yet been addressed.

The anoxic limestone drain is one component of the passive treatment system. When the ALD operates ideally, its only effect on mine water chemistry is to neutralize low pH and increase concentrations of calcium and bicarbonate alkalinity. Dissolved Fe and Mn should be unaffected by flow through the drain. The ALD must be

followed by a settling basin or wetland system in which metal precipitation reactions can occur. The type of post-ALD treatment system depends on the acidity of the mine water. An ALD rarely produces more than 300 mg/L alkalinity and many produce less than 200 mg/L alkalinity. Currently there are no design or construction guidelines that will ensure generation of a certain amount of alkalinity by an ALD.

In constructing a passive treatment system, one should determine if the net acidity of the initial influent mine water is less than 300 mg/L. If it is, it is likely that an ALD will add enough alkalinity to the water to make the effluent of the drain net alkaline. The drain effluent can then be treated with a settling basin and an aerobic wetland. If possible, the water should be aerated as soon as it exits the ALD and directed into a settling pond. Follow the settling pond with an aerobic wetland. Size the total post-ALD system according to the criteria provided earlier for net alkaline mine water.

If the net acidity of the initial influent water is greater than 300 mg/L, it is unlikely that an ALD would generate enough alkalinity to totally neutralize the acidity contained in this mine water. Building a second ALD, to recharge the mine water with additional alkalinity after it flows out of the aerobic system, is currently not feasible because of the high dissolved oxygen content of water flowing out of aerobic systems. If the treatment goal is to neutralize all of the acidity passively, then a compost wetland should be built so that additional alkalinity will be generated. Such a treatment system contains all three passive technologies. The mine water

flows through an ALD, into a settling pond and an aerobic system, and then into a compost wetland. Size the complete system based on removal of Fe in the aerobic section and removal of acidity in the anaerobic section, as explained in the next section.

$$\text{Minimal size (m}^2\text{)} = \frac{\text{Fe loading}}{20} + \frac{\text{Acidity Loading}}{5} \quad (5)$$

where the acidity loading is the net acidity of the ALD effluent. A preconstruction estimate of this value is obtained by subtracting 300 (the estimated alkalinity generated by the drain) from the original mine water acidity.

If Mn removal is desired, an additional aerobic wetland area is required after the compost wetland.

When DO, Fe³⁺ or Al are unacceptable for an ALD

Construction of a compost wetland is recommended. In many wetland systems, the compost cells are preceded with a single aerobic pond in which iron oxidation and precipitation occur. This feature is useful where the influent to the wetland is of circumneutral pH (either naturally or because of pretreatment with an ALD), and rapid, significant removal of iron is expected as soon as the mine water is aerated. Aerobic ponds are not recommended when the water entering the wetland system has a pH less than 4. At such low pH, iron oxidation and precipitation reactions are quite slow and significant removal of iron in the aerobic pond would not be expected.

Compost wetlands generate alkalinity through a combination of bacterial activity and limestone dissolution. The desired sulfate-reducing bacteria require a rich organic substrate in which anoxic conditions will develop. Limestone dissolution also occurs readily within this anoxic environment. A common substance used in these wetlands is spent mushroom compost, a substrate that is readily available in western Pennsylvania. However, any well-composted equivalent should serve as a good bacterial substrate. Spent mushroom compost has a high CaCO_3 content (about 10% dry weight), but mixing in more limestone may increase the alkalinity generated by CaCO_3 dissolution. Compost substrates that do not have a high CaCO_3 content should be supplemented with limestone.

The compost should be 12-18 inches deep. Experimental systems with greater depths of compost have been constructed, but it has not been determined whether higher rates of alkalinity generation occur. Most compost wetlands are planted with cattails by the same methods used in aerobic wetlands.

Compost wetlands in which water flows on the surface of the compost remove acidity (e.g. generate alkalinity) at rates of approximately 2-12 $\text{g/m}^2/\text{day}$. This range in performance is largely a result of seasonal variation; lower rates of acidity removal occur in winter than in summer (Hedin et al., 1991). There is recent evidence that supplementing the compost with limestone and incorporating system designs that cause most of the water to flow through the compost (as opposed to on the surface) may result in higher rates of limestone

dissolution and better winter performance (Hedin and Nairn, 1992).

The compost wetland system must be made large enough to precipitate the iron as a sulfide as well as raise the pH. Since dissolved iron is a component of acidity, experience has shown that sizing can be based on acidity alone. Study of alkalinity generation in compost wetlands indicates that acidity is removed at an average rate of 7 $\text{g/m}^2/\text{day}$. A conservative design estimate of 5 $\text{g/m}^2/\text{day}$ is recommended.

$$\text{Minimum Wetland Size (m}^2\text{)} = \frac{\text{Acidity Load}}{5} \quad (6)$$

CONCLUSIONS

There is no general solution to the problem of acidic drainage from mined lands. There are many options that can significantly reduce acid generation, such as inundation, alkaline addition and, for coal refuse, application of anionic surfactants (multiple refs). This paper has focused instead on water treatment, which is the means by which most mining operations meet their effluent requirements. Conventional AMD treatment is simple but expensive. The Bureau's research program has produced equally simple but less expensive treatment alternatives. Site characteristics determine whether any technique can be economically used at a specific site. Careful reading of this paper should allow you to evaluate these new options and decide among them. If you have doubts or concerns, please feel free to contact one of the authors for additional information.

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