A BRIEF OVERVIEW OF CONTROL AND TREATMENT TECHNOLOGIES
FOR ACID MINE DRAINAGE
WITH SPECIAL EMPHASIS ON PASSIVE SYSTEMS

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Abstract. Acid mine drainage (AMD) occurs when metal sulfides are exposed to oxidizing conditions. Leaching of reaction products into surface waters pollute over 20,000 km of streams in the USA alone. Mining companies must predict the potential of creating AMD by using overburden analyses. Where a potential exists, special handling of overburden materials and quick coverage of acid-producing materials in the backfill should be practiced. The addition of acid-neutralizing materials can reduce or eliminate AMD problems. Other AMD control technologies being researched include injection of alkaline materials (ashes and limestone) into abandoned underground mines and into buried acid material in mine backfills, and installation of alkaline recharge trenches. Chemicals used for treating AMD are Ca(OH)$_2$, CaO, NaOH, Na$_2$CO$_3$, and NH$_3$, with each having advantages under certain conditions. Floc, the metal hydroxide material collected after treatment, is disposed of in abandoned deep mines, refuse piles, or left in collection ponds, and recent work is identifying rare earth elements in floc. Passive AMD treatment relies on natural biological, chemical, and physical processes to neutralize acidity, and to oxidize and precipitate metal contaminants. Passive treatment technologies can be separated into biological types, which incorporate organic matter, and geochemical types that treat AMD through oxidation, precipitation and mineral dissolution. Biological passive treatment technologies generally utilize organic matter to adsorb contaminants and stimulate microbial sulfate reduction, and include constructed wetlands, vertical flow wetlands and bioreactors. Geochemical systems place alkalinity-generating materials such as limestone in contact with either AMD for direct treatment or with fresh water for indirect AMD treatment. Most passive treatment systems employ multiple methods, often in series, to promote acid neutralization, and oxidation and precipitation of the resulting metal flocs. Before selecting an appropriate passive treatment technology, the AMD conditions and chemistry must be characterized. Flow, acidity and alkalinity, metal, and dissolved oxygen concentrations are critical parameters.

Introduction

The purpose of this paper is to provide a brief overview of current acid mine drainage (AMD) control and treatment technologies for individuals not familiar with the AMD literature. The overview is primarily based on knowledge and experience with coal mining in the eastern U.S. Not all technologies are mentioned in this paper, nor are all the different situations where an AMD technology has been applied. Nevertheless, a few of the most promising technologies are reviewed. Some of the technologies are well known and have shown favorable control and treatment under almost all conditions, while others may be new and still being applied in various
Acid Mine Drainage Formation

Acid mine drainage (AMD) forms when sulfide minerals are oxidized in coal and metal mining, highway construction, and other large-scale excavations. Upon exposure to water and oxygen, sulfide minerals oxidize to form acidic products, which then can be dissolved in water. The water containing these dissolved products often has a low pH, high amounts of dissolved metals such as iron (Fe) and aluminum (Al), and sulfate. The metal concentrations in AMD depend on the type and quantity of sulfide minerals present, but the overall water quality from disturbed areas depends on the acid-producing (sulfide) and acid-neutralizing (carbonate) minerals contained in the disturbed rock. Therefore, sulfide-rich and carbonate-poor materials produce acidic drainage, while carbonate-rich materials produce alkaline conditions in drainage.

Approximately 20,000 km of streams and rivers in the United States are degraded by AMD. About 90% of the AMD reaching streams originates in abandoned surface and deep mines. Since no company or individual claims responsibility for reclaiming abandoned mine lands (AML), no treatment of the AMD occurs and continual contamination of surface and groundwater resources results.

The carbonate (and to a lesser degree, silicate) content of overburden determines whether there is enough neutralization potential (NP) to counteract the acid produced from pyrite oxidation. Of the many types of acid-neutralizing compounds present in rocks, only carbonates and clays occur in sufficient quantity to effectively neutralize acid-producing rocks. A balance between the acid-producing potential and neutralizing capacity of the disturbed overburden will indicate the ultimate acidity or alkalinity that might be expected in the material upon complete weathering. Control of AMD before surface mining requires an understanding of three important factors: 1) overburden geochemistry, 2) method and precision of overburden handling and placement in the backfill during reclamation, and 3) the post-mining hydrology of the site.

Overburden Analyses, Handling and Placement

Pre-mining analyses of soils, overburden, and the coal pavement are required by law (Sobek et al., 2000). Identifying the chemical production potential of overburden aids in developing overburden handling and placement plans by knowing which layers are potentially acid-producing, neutral, or acid-neutralizing. Acid-Base Accounting (ABA) provides a simple, relatively inexpensive, and consistent procedure to evaluate overburdens (Skousen et al., 1987). It balances potential acidity (based on total or pyritic sulfur content) against total neutralizers. Samples containing more acid-producing than acid-neutralizing materials are deficient in neutralizing materials (“maximum needed”), and those samples with the reverse situation have "excess" neutralizing materials. Rock layers with equal proportions of each type of material should be subjected to leaching or weathering analyses (Kleinmann, 2000). Kinetic tests such as humidity cells and leach columns are important because they examine the rate of acid-producing and neutralization reactions. This information from kinetic tests can supplement information given by ABA and help regulators in permitting decisions (Geidel et al., 2000).

The prevailing approach to control AMD in the eastern USA is to keep water away from pyritic material. Once overburden materials have been classified, an overburden handling and placement plan for the site can be designed. Segregating and placing acid-producing materials above the water table is generally recommended (Skousen et al., 1998). Where alkaline materials
overwhelm acid-producing materials, no special handling is necessary. Where acid-producing materials cannot be neutralized by on-site alkaline materials, it is necessary to import a sufficient amount to neutralize the potential acidity or the mining activity may not be allowed. Often, an excess of neutralizing materials (sometimes up to two to three times the potential acidity) is required to offset the acid formation.

Post-mining Hydrology

The hydrology of a backfill and its effect on AMD are very complex. Generally, the porosity and hydraulic conductivity of the materials in a backfill are greater than those of the consolidated rock overburden that existed before mining, and changes in flow patterns and rates should be expected after mining (Caruccio and Geidel, 1989). Water does not move uniformly through the backfill by a consistent wetting front. As water moves into coarse materials in the backfill, it follows the path of least resistance, e.g., through more permeable sandstones and around shales. The water continues downward until it encounters a barrier, the coal pavement, or other compacted layer. Therefore, the chemistry of the water from a backfill will reflect only the rock types encountered in the water flow path, and not the entire geochemistry of the total overburden (Ziemkiewicz and Skousen, 1992).

Diverting surface water above the site to decrease the amount of water entering the mined area is highly recommended. Pyritic material can be placed where it will be rapidly and permanently inundated, thereby preventing oxidation. Inundation is only suggested where a water table may be re-established such as below drainage deep mines. Above mined areas, incoming water can be treated with limestone to improve water quality.

Control of AMD

Acid mine drainage control can be undertaken where AMD exists or is anticipated. At-source control methods treat the acid-producing rock directly and stop or retard the production of acidity, whereas treatment methods add chemicals directly to acidic water exiting the rock mass. Coal companies mining in acid-producing areas of the eastern USA must often treat AMD, and they face the prospect of long-term water treatment and its attendant liabilities. Cost-effective methods, which prevent the formation of AMD at its source, are preferable and mandated by regulatory authorities for permit issuance. Some control methods are most suited for abandoned mines and others are only practical on active operations. Other methods can be used in either setting.

Some techniques described below have demonstrated less than 100% control of acidity produced on-site, and are considered failures by some people. Removing a significant portion of the acid or metal load in a watershed by a control strategy may improve the health of a stream to a point of re-introducing some fish species or re-establishing some designated uses of the stream. Alternatively, the method may be combined with another partial control schemes to achieve effluent limits. Since partial control methods are often the least costly, their use in combination with other techniques is financially attractive.

Land Reclamation

Backfilling and revegetation together are effective methods of reducing acid loads from current mining operations or abandoned mine lands. Backfilling alone can reduce the acid load
substantially or improve water quality to the point of meeting effluent limits (Faulkner and Skousen, 1995). Water flow from seeps can be reduced by diversion and reclamation, and on some sites where flow may not be reduced, water quality can change from acid to alkaline. Diverting surface water or channeling surface waters to control volume, direction and contact time can be used to minimize the effects of AMD on receiving streams. Surface diversion involves construction of drainage ditches to move surface water quickly off the site before infiltration or by providing impervious channels for existing streams to convey water across the disturbed area.

Alkaline Amendment to Active Mines

Certain alkaline amendments can control AMD from spoil and refuse (Brady et al., 1990; Perry and Brady, 1995; Rich and Hutchison, 1990; Rose et al., 1995). All alkaline amendment schemes rely on ABA or kinetic tests to identify the required alkalinity for neutralization of pyritic materials. Special handling of overburden seeks to blend acid-producing and acid-neutralizing rocks in the mining process to develop a neutral rock mass. In the eastern USA, the pit floor is often rich in pyrite, so isolating it from groundwater may be necessary by building highwall drains (which move incoming groundwater away from the pit floor) or placing impermeable barriers on the pit floor. Acid-forming material can be compacted or capped within the spoil (Meek, 1994).

If insufficient alkalinity is available in the spoil, then external sources of alkalinity must be imported (Skousen and Larew, 1994). Limestone is often the least expensive and most readily available source of alkalinity (Wiram and Naumann, 1995). Other alkaline materials can be used such as fly ashes, Fluidized Bed Combustion (FBC) ash (Skousen et al., 1997a), Flue Gas Desulfurization (FGD) products and scrubber sludges (Stehouwer et al., 1995), Kiln Dust (Rich and Hutchison, 1994) and Steel Slags (Ziemkiewicz, 1998).

Chemical Treatment of AMD

If AMD problems develop during mining or after reclamation and if discharge limits are exceeded, a plan to treat the discharge must be developed. Treatment of AMD includes neutralization of acidity and precipitation of metal ions to meet the relevant effluent limits. In most cases, a variety of alternative treatment methods can be employed to meet the effluent limits specified in NPDES permits. At a minimum, pH, total suspended solids (TSS), iron, aluminum, and manganese concentrations are regulated. Other parameters are normally required by the regulatory authority in a particular mining situation. However, in order for an operator to make a selection of an AMD treatment system, one must determine (in addition to the above parameters) the flow rate, the receiving stream’s flow and quality, availability of electrical power, the distance from chemical addition to where the water enters a settling pond, and the settling pond’s volume for water retention time. After evaluating these variables over a period of time, the operator can consider the economics of different chemicals and alternative AMD treatment systems. Special circumstances like the treatment of trace elements in the water (like selenium or arsenic) may require a specialized treatment system that includes filtration techniques or reverse osmosis (Sandy, 2010), which are generally much more expensive to install and operate than traditional alkaline addition and precipitation.

Chemicals primarily used to treat AMD are Hydrated Lime (Ca(OH)₂), Quicklime (CaO), Ammonia (NH₃), and Caustic (NaOH). Each is more or less appropriate for a specific condition.
The best choice depends on both technical (acidity levels, flow, and the types and concentrations of metals) and economic factors (chemical prices, labor, machinery and equipment, treatment duration, and interest rates). Enough alkalinity must be added to raise pH to between 6 and 9 so insoluble metal hydroxides will form and settle out. Treatment of AMD with high Fe (ferric) concentrations often affords co-precipitation of other metals with the Fe hydroxide, thereby removing them from AMD at a lower pH.

After chemical treatment, the treated water flows into sedimentation ponds so metals in the water can precipitate. All AMD treatment chemicals cause the formation of metal hydroxide sludge or floc. Sufficient residence time of the water (dictated by pond size and depth) is important for adequate metal precipitation. The amount of metal floc generated depends on water quality and quantity, which in turn determines how often the ponds must be cleaned. Knowing the chemical and AMD being treated will provide an estimate of the stability of metal compounds in the floc. Floc disposal options include: 1) leaving it submerged indefinitely in the pond, 2) pumping or hauling it to abandoned deep mines or to pits dug on surface mines, and 3) dumping it into refuse piles. Pumping flocs onto land and letting them age and dry is a good strategy for disposal, because they become crystalline and behave like soil material.

Each AMD is unique, requiring site specific treatment. Each AMD source should be tested with various chemicals by titration tests to evaluate the most effective chemical for precipitation of the metals. The costs of each AMD treatment system based on neutralization (in terms of the reagent cost, capital investment and maintenance of the dispensing system) and floc disposal should be evaluated to determine the most cost-effective system.

**Passive Treatment of AMD**

Active chemical treatment of AMD is often an expensive, long-term proposition. Passive treatment systems have been developed that do not require continuous chemical inputs and that take advantage of natural physical, chemical and biological processes to improve water quality. Primary passive technologies can be broadly divided into biological systems with organic matter and geochemical systems containing inorganic materials, primarily carbonates. The biological systems include aerobic and anaerobic constructed wetlands (AeW and AnW), vertical flow wetlands (VFW), and bioreactors. The geochemical systems include anoxic limestone drains (ALD), open limestone channels (OLC), limestone leach beds (LLB), steel slag leach beds (SLB), diversion wells, low pH Fe-oxidation channels, and limestone sand.

Selection of an appropriate passive system is based on water chemistry, flow rate, and local topography and site characteristics. Figure 1 (modified from Hedin et al. 1994) summarizes a strategy for selecting the appropriate type of passive system and Table 1 gives recommended sizing criteria. In general, AeWs are effective for removing metal precipitates from net-alkaline mine drainage. ALDs can treat acidic water with low Al, Fe$^{3+}$, and dissolved oxygen (DO); and VFWs, AnWs, flushable LLBs and OLCs can treat net-acidic water with higher Al, Fe$^{3+}$, and DO. The science and technology supporting passive systems is increasing. Hence, their capacity to treat more difficult waters with appropriate designs and size is also improving.
Figure 1. Flow chart for selecting a passive AMD treatment system based on water chemistry and flow (adapted from Hedin et al. 1994).

Biological Systems

Aerobic wetlands consist of wetland vegetation in shallow (<30cm), relatively impermeable sediments comprised of soil, clay or mine spoil. Anaerobic wetlands consisting of wetland vegetation in deep (>30cm), permeable sediments comprised of soil, peat moss, spent mushroom compost, sawdust, straw/manure, hay bales, or other organic mixtures, often underlain or admixed with limestone. Metals are retained within wetlands by 1) formation of metal oxides and oxyhydroxides, 2) formation of metal sulfides, 3) organic complexation reactions, 4) exchange with other cations on negatively-charged sites, and 5) direct uptake by living plants. Metals can also be retained by filtration and adsorption/exchange. Other beneficial reactions in wetlands include generation of alkalinity due to microbial mineralization of dead organic matter, microbial dissimilatory reduction of Fe oxyhydroxides and SO$_4$, and dissolution of carbonates.

Aerobic wetlands promote metal oxidation and hydrolysis, thereby causing precipitation and physical retention of Fe, Al, and Mn oxyhydroxides. Successful metal removal depends on dissolved metal concentrations, dissolved oxygen content, pH and net acidity of the mine water, the presence of active microbial biomass, and detention time of the water in the wetland. The pH and net acidity/alkalinity of the water are particularly important because pH influences both the
solubility of metal hydroxide precipitates and the kinetics of metal oxidation and hydrolysis. Therefore, aerobic wetlands are best used in conjunction with water that contains net alkalinity to neutralize metal acidity.

Anaerobic wetlands are most successful when used to treat small flows of acidic water. Anaerobic wetlands use chemical and microbial reduction reactions to precipitate metals and neutralize acidity. The water infiltrates through a thick permeable organic subsurface that becomes anaerobic due to high biological oxygen demand. Other chemical mechanisms that occur in-situ include metal exchanges, formation and precipitation of metal sulfides, microbial-generated alkalinity, and formation of carbonate alkalinity (due to limestone dissolution). Since anaerobic wetlands produce alkalinity, they can be used in net acidic and high dissolved oxygen (>2 mg/L) AMD. Microbial mechanisms of alkalinity production are critical to long-term AMD treatment. Under high acid loads (>300 mg/L), pH sensitive microbial activities are eventually overwhelmed. At present, the sizing value for Fe removal in these wetlands is 10 grams per day per meter squared (Hedin and Nairn, 1992).

Like their aerobic counterparts, AnWs are most successful when used to treat small AMD flows of moderate acidity. Sizing criteria for AnWs have been based on incoming Fe load (10 g m\(^{-2}\) d\(^{-1}\), Hedin and Nairn, 1992) or acid load (3.5 g m\(^{-2}\) d\(^{-1}\), Hedin et al., 1994). Ziemkiewicz et al. (2003) showed that 17 AnWs removed acidity at an average rate of 16.6 g m\(^{-2}\) d\(^{-1}\).

Vertical flow wetlands (VFW) were developed in the late 1980s (Hendricks 1991) and described by Duddleston et al. (1992) and Kepler and McCleary (1994, 1997). In a VFW, acidic water is ponded to a depth of 1 to 2 m over 0.2 to 0.6 m of an organic substrate which rests on a 0.5 to 1 m layer of limestone. The hydraulic head of the ponded water drives it through the organic substrate, where O\(_2\) is consumed to produce anoxic conditions where metals and SO\(_4^{2-}\) are reduced. The major function of the organic layer is reduction of all Fe to Fe\(^{2+}\) which prevents coating of the underlying limestone with ferric hydroxide. Acid neutralization occurs in the organic layer and in the limestone base. A series of perforated drainage pipes below the limestone conveys the water into an aerobic wetland or settling pond where Fe and Mn are precipitated. Initially, these systems were sized to allow 16 to 24 hours of retention time in the limestone layer as recommended by Hedin et al. (1994) for ALDs (see below), but studies of performance indicated that an areal sizing parameter was required (Rose 2006). As a result, many early VFWs were not adequately sized to treat their inflow.

**Bioreactors**

Bioreactors, which are sometimes called sulfate-reducing bioreactors (SRBR), are similar to VFWs except that organic matter is the main reactant, commonly with limestone completely mixed with the organic matter. Microbial sulfate reduction is the primary form of treatment (Neculita et al. 2007; Rose, 2004). These systems are capable of handling very acidic and metal-rich water, including mine drainage with transition and heavy metals. However, flow rates through these systems are slow, so they are most applicable to small flows or to situations where multiple units can be operated in parallel. Most units are used for treatment of effluent from waste or tailings at metal mines to capture the heavy metals, but a few have been used for coal mine effluent.
Anoxic Limestone Drains

Anoxic limestone drains (ALDs) are buried beds or trenches of limestone into which anoxic water is introduced. The limestone raises pH and adds alkalinity. Under anoxic conditions, the limestone does not coat or armor with Fe hydroxides because Fe$^{2+}$ does not precipitate as Fe(OH)$_2$ at pH 6.0. Faulkner and Skousen (1994) reported both successes and failures among 11 ALDs with water pH being raised in all cases but Fe and Al were being retained inside the ALD. Longevity of treatment is a major concern for ALDs, especially in terms of water flow through the limestone. Selection of the appropriate water and environmental conditions is critical for long-term alkalinity generation in an ALD. Eventually clogging of the limestone pore spaces with precipitated Al and Fe hydroxides, and gypsum is predicted (Nairn et al., 1991). For optimum performance, no Fe$^{3+}$, dissolved oxygen (DO), or Al should be present in the AMD. Like wetlands, ALDs may be a solution for AMD treatment for specific water conditions or for a finite period after which the system must be replenished or replaced.

Open Limestone Channels

Open limestone channels (OLCs) introduce alkalinity to acid water (Ziemkiewicz et al., 1994). A coating of Fe generally develops on the limestone surface and slows dissolution, but Ziemkiewicz et al. (1997) found armored limestone to be 50 to 90% effective in neutralizing acid compared to unarmored limestone. Open limestone channels show promise for neutralizing AMD in watershed restoration projects and AML reclamation projects where there can be only a one-time installation cost, little to no maintenance is required, and water exiting the system does not have to meet water quality standards. Long channels of limestone can be used to convey acid water to a stream or other discharge point. Cross sections of channels can be designed with calculated amounts of limestone (which will become armored) to treat the water. Open limestone channels work best on steep slopes (>20%) where flow velocities keep metal hydroxides in suspension, thereby limiting plugging. If constructed correctly, OLCs should be maintenance free and provide AMD treatment for decades.

Limestone Leach Beds

Limestone leach beds (LLB) are small basins filled with coarse limestone rock and designed to provide a maximum 30 minutes of water residence time. If AMD is allowed to enter, the limestone gets coated with metal hydroxides, thereby reducing its dissolution rate (Ziemkiewicz et al. 1997). Therefore, LLBs work best in low pH, metal-free water, and can add alkalinity to streams before encountering acid water downstream (Ziemkiewicz et al., 2001). LLBs can be fully passive or activated by self-flushing mechanisms.

Steel Slag Leach Beds

Steel slag is a byproduct of steel production. Steel slag leach beds (SLB), first described by Ziemkiewicz (1998) and Ziemkiewicz and Skousen (1998), use steel slag as a cost-effective alternative to limestone-based passive systems. Steel slag is available from metal recovery operations which mine old slag piles and grind the slag into sand to fine gravel sizes. Steel slags have high neutralization potentials (from about 50-70%), can generate exceptionally high levels of alkalinity in water (Ziemkiewicz and Skousen, 1998). SLBs are effective for generating strongly alkaline water in settings where metal-free feed water is available. The alkaline water
from these systems can then be mixed with AMD for treatment. Metal-laden water should not be used with finely ground steel slag since the slag will become clogged with metal precipitates almost immediately.

**Limestone Sand Treatment**

Limestone sand treatment is the addition of sand-sized limestone to streams in a watershed (Zurbuch, 1996). The sand is picked up by the streamflow and redistributed downstream, neutralizing acid as the energy of the stream transports the limestone into the streambed. Coating of limestone particles with Fe hydroxides can occur, but the energy of the water in the stream causes scouring by stream sediments to keep fresh limestone surfaces available for reaction.

**Low-pH Iron Oxidation Channels**

Low-pH Fe oxidation channels are shallow channels constructed and lined with limestone to enhance Fe oxidation and to promote adsorption and co-precipitation on rocks in conjunction with Fe-oxidizing bacteria. At pH 4.5, Fe oxidation is very slow, but at pH below 3.5 Fe oxidation can be catalyzed by specialized bacteria. A number of sites where this occurs naturally have been identified. At these sites, channel slopes and wide flow paths enable adequate air contact. In the process, Fe$^{2+}$ is oxidized to Fe$^{3+}$, some of which precipitates and thereby decreases dissolved metal concentrations. At some sites, nearly all dissolved Fe was removed. The low-pH oxidation channels provide some Fe removal where conditions can be met, but removal efficiencies have not yet been determined.

**Summary**

Acid mine drainage occurs when metal sulfides are oxidized. Leaching of reaction products into surface waters pollute over 20,000 km of streams in the USA alone. Companies must predict AMD before mining by using overburden analyses. On sites where a potential exists, special handling of overburden materials and quick coverage of acid-producing materials in the backfill should be practiced. Alkaline addition with materials such as kiln dust and FBC ash can reduce or completely eliminate AMD problems. Other control techniques include barriers and adding alkaline materials. Chemicals are used to treat AMD and each has characteristics that make it suitable for specific applications. Companies must select a chemical that treats the water adequately and cost-effectively. Passive systems are low maintenance systems that are implemented on abandoned mine land and stream restoration projects. Certain systems are more suited to specific water quality and show good success where the acid levels do not overwhelm the system.

**References**


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