Restoration and Reclamation Review
Student On-Line Journal
Vol.5, No.1, Fall 1999
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Acid Mine Drainage In Pennsylvania Streams: "Ironing Out" The Problem

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Introduction

Acid mine drainage (AMD) is a national problem, but one-third of waters impacted by that problem are located in Pennsylvania, which, after over a century of coal extraction, has produced more coal tonnage than any other state in the U.S. AMD is Pennsylvania's single largest non-point source water pollutant, impacting 2500 miles of streams (PA DEP, 1999b).

AMD is formed when mining activities expose pyrite (iron disulfide minerals) to water and oxygen. Upon exposure to water and oxygen,.pyrite oxidizes to form acidic drainage rich in dissolved metals. The chemical reactions that occur during the formation of AMD can be summarized as this overall reaction:

$$4\ FeS_2 + 15\ O_2 + 14\ H_2O \rightarrow 4\ Fe(OH)_3^- + 8\ H_2SO_4.$$

In this reaction, pyrite is oxidized to give ferrous hydroxide (or "yellowboy", that creates the characteristic rust color of AMD contaminated streams) and sulfuric acid. The presence of sulfides also stimulates *Thiobacillus*, sulfide-consuming bacteria that releases H_2SO_4 as a by-product, further increasing acidity. AMD water is characterized by low pH (<3.5), high acidity (>500 mg/l as $CaCO_3$), and high concentration of total dissolved metals (>50mg/l) (Ziemkiewicz et al. 1997).

Untreated AMD can severely degrade both habitat and water quality of receiving streams (Kimmel 1983). This degradation is manifested by an alteration in the macroinvertebrate community; specifically, there is a reduction in the diversity and total numbers of macroinvertebrates and massive shifts in community structure, favoring pollution tolerant species. In addition to the stress posed by a less abundant food source, fish are also negatively impacted by AMD directly. The primary causes of fish death in acid waters are loss of sodium ions from the blood and loss of oxygen in the tissues (Brady et al. 1988). AMD contaminated groundwater can corrode and encrust man-made structures, causing serious problems. For example, AMD can compromise well casings (water supply or oil and gas wells) which can lead to aquifer contamination (Merrit and Emrich 1970). In the most severe cases, AMD renders waters unfit for human use and recreation.

The Appalachian Mountain range spans several states along the eastern coast of the United States, including Pennsylvania in the northeast part of the country. Terrestrial depositional environments of ca. 300 million years ago left Pennsylvania (and other parts of the Appalachian region) rich in coal-bearing sedimentary rock. The long-term and ubiquitous nature of mining in Pennsylvania has resulted in numerous AMD discharge sites across the state. Therefore, focusing on Pennsylvania's AMD remediation history provides a useful framework for a thorough review of AMD remediation techniques.

Mining was unregulated in the U.S. until 1965, when Pennsylvania's Clean Streams Law was modified to regulate discharges from coal mining operations (PA DEP 1999c). Nationally, the Surface Mining Control and Reclamation Act of 1977 and the Clean Water Act of 1972 required mining operations to obtain a permit to treat water for AMD before it is discharged into natural aquatic ecosystems. However, this did not prevent Pennsylvania's Department of Environmental Protection (PA DEP) from issuing mining permits for operations that would continue to discharge poor quality water after the completion of mining. In 1984, PA DEP incorporated into the mining permit process the submission of scientific data to be used to assess a site's potential to generate AMD. From 1987-1996, only 17 out of 1,699 permits, or 1 percent of the total permits issued, were considered to have caused long-term post-mining discharges above effluent limits (PA DEP 1999b).

Although permitted projects do not contribute significant AMD, thousands of other Pennsylvania mines abandoned prior to the passage of water quality laws, or operated by companies which dissolved or went bankrupt, discharge untreated AMD directly into receiving water systems (Hedin 1989). These sites fall under the jurisdiction of PA DEP's Bureau of Abandoned Mine Reclamation, which administers the abandoned mine lands (AML) reclamation program in Pennsylvania. Each year the Bureau receives more than 800 requests for assistance with potential abandoned mine problems; most of these requests are from private property owners. Each request is investigated to determine if the site is eligible for funding. Approximately 30% of these requests are eligible for reclamation, which is dependent upon a number of factors including economic and technologic feasibility, the degree of hazard caused to human and environmental health, and the lack of reclamation responsibility of any mine operation.

AMD Remediation

Mine operators and the Bureau of Abandoned Mine Reclamation use several AMD remediation techniques, often in combination. The fundamental goals of remediating AMD waters are to: 1) raise the pH of effluent, and 2) remove metal concentrations of the effluent. Chemical treatment, which is expensive and requires frequent maintenance (Ziemkiewicz et al., 1997), is currently the most common remediation technology. Alternatives to chemical treatment, such as constructed wetlands and limestone channels are becoming more standard, mostly because of their economic benefits.

New AMD bioremediation techniques are currently being researched and developed. For example, microbial mitigation reactors use microbial cultures in reactors to remove AMD-related contaminants, and the use of site-specific cultured microbes to passively treat AMD-contaminated water are two promising techniques.

Chemical Treatment

Chemical treatment systems are the standard remediation technique for treatment of AMD, and treat water with additions of highly alkaline chemicals such as $NaOH$, $Ca(OH)_2$, CaO, Na_2CO_3, or NH_3 (Skousen et al., 1990). The mechanism of these systems is to raise the pH of the effluent until metals are precipitated and can settle out in a retention pond. AMD chemical treatment systems consist of an inflow pipe or ditch, a storage tank or bin holding the treatment chemical, a means of controlling chemical application rate, a settling pond to capture precipitate metal oxyhydroxides, and a discharge point (Skousen et al. 1999). The amount of chemical needed to neutralize acidity is calculated as the amount of acidity in effluent over a year's time (tons/year) multiplied by a chemical specific conversion factor (see Table 1).

Chemical treatment of acid mine drainage required to maintain effluent within legal limits was estimated at $1 million per day in the Appalachian area in 1987 (Kleinmann and Girts 1987). Of the eight chemicals used most frequently, cost varies widely (Table 1, Skousen et al. 1999).

Table 1. Chemical compounds used in AMD treatment (from Skousen et al. 1999).

Common name	Chemical name	Formula	Conversion factor	1996 cost ($/ ton or gallon)
Limestone	Calcium carbonate	$CaCO_3$	1	$15
Pebble quicklime	Calcium oxide	CaO	0.74	$240
Hydrated lime	Calcium hydroxide	$Ca(OH)_2$	0.56	$100
Soda ash	Sodium carbonate	Na_2CO_3	1.06	$320
Caustic soda (solid)	Sodium hydroxide	NaOH	0.8	$880
20% liquid caustic	Sodium hydroxide	NaOH	784	$0.60
50% liquid caustic	Sodium hydroxide	NaOH	256	$1.25
Ammonia	Anhydrous ammonia	NH_3	0.34	$680

The selection of a treatment chemical depends on characteristics of the effluent (pH, iron and manganese concentrations), and also on the flow rate, the receiving stream's flow and quality, the availability of electrical power, the distance from chemical addition to where the water enters a settling pond, and the settling pond's retention time.

Although chemical treatment is often very efficient in promoting metal removal and neutralizing acidity, the chemicals are expensive, dangerous, and when misused can result in discharge of excessively alkaline water (Hedin et al. 1994).

Passive Treatment

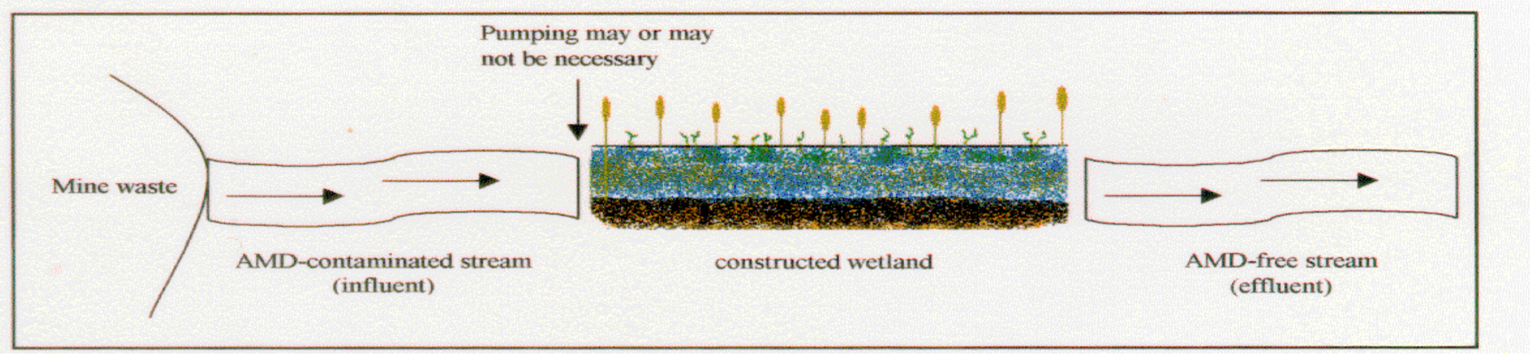
Passive treatment refers to any little or no maintenance treatment of acid mine drainage that does not require continual chemical addition and monitoring. Wetlands have received particular attention because processes within wetlands can precipitate and remove metals. Limestone drains, wetlands, or a combination of both are the most often used passive treatment system (Faulkner and Skousen 1994). Passive treatments are discussed below.

Constructed Wetlands

Interest in aerobic wetlands as possible passive treatment was generated as a result of observations that natural *Sphagnum* peat wetlands that received AMD improved water quality without any obvious adverse ecological effects (Hedin 1989). Discharge of polluted waters into natural wetlands, however, is prohibited in the United States, so wetlands are constructed specifically for the purpose of treating AMD. Early efforts to treat AMD with constructed wetlands mimicked the *Sphagnum* peat wetland model. Lab experiments suggested promising results (Kleinmann et al. 1983, Gerber et al. 1985), but *Sphagnum* proved to be very sensitive to transplanting stress, abrupt changes in growing conditions, and excessive accumulation of iron (Hedin 1989).

The current conventional design of wetlands constructed to treat AMD looks nothing like a *Sphagnum* wetland, although the same processes are used to treat water. Constructed wetlands consist of a series of cells that allow hydrology to be easily controlled to maximize treatment effectiveness. AMD treatment wetlands are planted with *Juncus, Eleocharis, Scirpus,* and *Typha,* although *Typha latifolia* (common cattail) is used most often (Hedin 1989, Brodie et al. 1992). Vegetation is planted into an organic substrate such as topsoil, rotten animal manure, spoiled hay, and compost. Water flow is slow, with a depth of 15-45 cm. Wetlands can be constructed at the discharge point of AMD contaminated streams (see Figure 1), or AMD contaminated waters can be pumped into a more convenient wetland construction site (PA DEP 1999c).

Figure 1. The placement of a constructed wetland with respect to mine waste and AMD



contaminated stream.

The principal mechanism of metal removal in constructed wetlands is oxidation catalyzed by microbes. Iron drains from mining activities in the reduced ferrous form, which eventually oxidizes and hydrolyses to insoluble iron oxyhydroxides, which precipitate and settle out. Aerobic chemoautotrophic and chemoheterotrophic microbes increase the ferrous iron oxidation rate by several orders of magnitude. Numbers of iron-oxidizing bacteria have been positively correlated with iron removal from experimental wetland systems (Stone 1984).

Aerobic wetlands are sized based on criteria under the Abandoned Mined Lands (AML) regulation. AML criteria for sizing constructed wetlands is based on this formula:

$$\text{Minimum wetland size (ac)} = 180_{(\text{lb/ac/day})}\ (\text{Fe loading}_{(\text{lb/day})}) + 9_{(\text{lb/ac/day})}\ (\text{Mn loading}_{(\text{lb/day})}) + 60_{(\text{lb/ac/day})}\ (\text{Acidity}_{(\text{lb/day})})$$

Constructed wetlands are efficient when the effluent is low in its acidity loading, but often show reduced efficiency and even fail under high acid loading (Kleinmann et al. 1991). For this reason, alkalinity additions to wetland influent may precede constructed wetlands (see following sections on open limestone channels and anoxic limestone drains).

Compost (or anaerobic) wetlands utilize similar microbial processes as constructed wetlands, but are more saturated to create more anaerobic zone area, and may or may not contain plants. These wetlands, which use compost as an organic substrate, can handle moderate acidity loadings (about 500mg/L), and may not require any alkalinity additions before precipitating metals (PA DEP 1999c).

Open Limestone Channels

In coal mining regions, limestone is prevalent and therefore is the least expensive buffer material. This led to construction of open limestone channels to pre-treat AMD effluent. Open limestone channels raise the pH of effluent by the reaction of calcite with carbonic acid:

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^{-}.$$

Complications arise when the Fe^{3+} and Al present in AMD are exposed to the atmosphere, forming metal hydroxides (e.g. $Fe(OH)_3$) and resulting in a surface coating of the limestone channel known as armoring. This coating reduces limestone pore space, decreasing the limestone solubility and acid neutralization effect (Ziemkiewicz et al. 1994). Large quantities of limestone are needed to generate the alkalinity to ensure long-term success of open limestone channels, but high flow velocity and turbulence keep precipitates in solution and reduce the armoring effect and the quantities of limestone needed (PA DEP 1999c).

Ziemkiewicz et al. (1994) found that armoring rendered open limestone channels almost totally ineffective. It has since been suggested that if the channels are constructed correctly, open limestone channels should be maintenance free and provide AMD treatment for decades. Channels constructed with steep slopes (>20%) and with flow velocities that keep metal hydroxides in suspension showed that the drains were only 2-45% less effective when armored (Ziemkiewicz et al. 1997). Although open limestone channels suggest a promising remedition technique, more research is needed to test the effects of armoring on different characteristics of AMD effluent.

Anoxic Limestone Drains (ALDs)

Turner and McCoy (1990) demonstrated that if mine water contacted the limestone in an anoxic environment, armoring would not occur. In their study, AMD water containing iron and manganese was channeled through an underground limestone-lined trench, became alkaline, and was discharged into wetlands where the metal contaminants were then precipitated. These structures, known as anoxic limestone drains (ALDs), were constructed throughout Appalachian coal mining areas. The rise in pH of ALD treated effluent occurs due to the principle bicarbonate-producing process that occurs in open limestone channels, the reaction of calcite with carbonic acid.

Although ALDs are documented to have success in raising pH, they have shown large variation in generating alkalinity and removing metals (Faulkner and Skousen 1993). Causes of this variation in alkalinity generation and retention of metals are likely a result of differing chemical characteristics of the influent mine water (Hedin et al. 1994).

Microbial Mitigation Reactors

Studies have shown that microorganisms in microbial mitigation reactors are capable of remediating AMD contaminated waters by both raising pH and removing metals (Mills 1985, Cairns et al. 1988). These reactors consist of a plastic container filled with a cellulosic material (most often straw), with an influent pipe and an effluent pipe (Bechard et al. 1994). Most of the cellulosic material is under anaerobic conditions, but the top layer is aerobic. Experimental microbial mitigation reactors were limited by C, and required a periodical addition of sucrose to stimulate microbial activity over an extended period of time. Therefore microbial mitigation reactors were not considered a self-sustaining treatment (Bechard et al. 1993).

Bechard et al. (1994) showed that simply modifying the straw substrate of the microbial systems eliminated the need to add a sucrose amendment. Using alfalfa as a substrate, which has a lower C:N ratio (13:1) than straw (60:1), provided more C to the system. Microbial mitigation reactors that use alfalfa as a substrate could be low maintenance treatment systems. More research is needed across varying AMD water characteristics to determine feasibility of this technique.

Pyrolusite Process

The Pyrolusite patented process was developed at Frostburg State University, Maryland. It uses limestone chips to neutralize acidity and then site-specific laboratory cultured microbes to remove metals. Laboratory testing determines the proper combination of different microbes for a particular site, and the microbes are innoculated throughout a shallow bed of chipped limestone at several innoculation ports. The microbes oxidize the metal contaminants from the surface of the limestone chips. This bioremediation technique has been successfully used on several sites in western Pennsylvania (PA DEP 1999c).

Vertical Flow Reactors

Vertical flow Reactors (VFRs) were constructed as an alternative to a combined ALD and constructed wetland system (PA DEP 1999b). VFRs overcome the alkalinity producing limitations of ALDs and require much less area than constructed wetlands. A VFR consists of one underground treatment cell, which is lined with a limestone base. Water snakes vertically through pipes that expose the effluent to alternating compost and limestone. Effluent is then discharged into a settling pond. VFRs are a new technology and are not a standard AMD remediation technique, but they have shown success in several cases (PA DEP 1999b).

Conclusion

Given the expense and the unpredictable nature of remediating AMD contaminated waters with chemical treatment systems, research on alternative methods of remediation is very justified. Passive treatment methods show promising results, particularly constructed wetlands and ALDs and combinations of these treatments (Hedin et al. 1994). It is, however, difficult to generalize about the success of any particular remediation technique across multiple site situations.

Evaluating AMD techniques is complicated because the characteristics of AMD contaminated waters are based on site conditions and are extremely variable, and therefore require unique remediation methods. One conclusion applies to all AMD treatment situations: because AMD generation may continue for centuries after a mine closure, remediation techniques should be low maintenance and low cost. A low cost, low maintenance remediation plan can be based on a combination of techniques, and requires extensive site analysis to determine the best alternative. Table 2 gives three examples of recently completed AMD abatement projects and the AMD techniques chosen. All projects used passive treatment.

Table 2. Recently completed AMD abatement projects in Pennsylvania (PA DEP, 1999a).

site	**Type of AMD remediation used**	**Success reported**
Cucumber Run Fayette County, PA	2 ALDs discharging into a constructed wetland	Very effective: Acidity has dropped to near 0 at wetland effluent, Fe has been reduced from 150mg/l to <2.5mg/l, Al has been reduced from 20mg/l to 1mg/l.
Laurel Run Westmoreland County, PA	Pyrolusite process	Very effective: pH increased from 3 to 7, Fe has been reduced from 4mg/l to <0.1mg/l, Al has decreased from10mg/l to <0.5mg/l
Schrader Creek Bradford County, PA	2 vertical flow wetland systems	Not effective yet, but looks promising (has only been operating for 1 month): pH has increased from 3 to 6, already low iron levels have been reduced to 1.5mg/l and less.

Selecting AMD treatment techniques for a particular site requires extensive analysis of site characteristics, which is part of the PA DEP mine permitting process. Due to the variable nature of AMD contaminant concentrations and mixtures, and the difficulty of translating between lab and field, predicting the most efficient remediation technique is complicated, even with substantial data. One way that future AMD abatement projects could be guided in their choice of remediation techniques is by consulting the successes and failures of already completed AMD abatement projects.

AMD abatement projects are carried out by a variety of mining operations and Pennsylvania DEP personnel, and there is no centralized medium for collecting timely information about completed AMD remediation projects. The mining permitting process requires that mining operations report reclamation successes and failures. This requirement could be extended to include posting reclamation data on a Pennsylvania DEP website that summarizes completed AMD abatement projects. Posted information would include data summarizing the site hydrogeology, the pre-treatment effluent characteristics, the post-treatment effluent characteristics (and the time from initial treatment to measurement), and the remediation technologies used. By observing the plans of projects with similar site and effluent characteristics, future AMD abatement projects could use the website as a valuable tool for AMD remediation planning.

Acknowledgements

Helpful reference documents for this paper were provided by Colleen Stutzman and the Pottsville Office of the District Mining Operations for the Pennsylvania Department of Environmental Protection.

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