

FINAL DRAFT REPORT

PASSIVE AND SEMI-ACTIVE
TREATMENT OF ACID ROCK
DRAINAGE FROM METAL MINES
- STATE OF THE PRACTICE

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This document presents an overview of current state-of-the-practice applications for passive and semi-active treatment systems to treat acid rock drainage (ARD) associated with metal mines. Acid rock drainage is a common effluent of metal mining and one of the major environmental impacts resulting from mining activities. It is caused by the natural weathering of pyrite and other metal sulfides in the mineral deposit, or through the accelerated weathering of waste products generated by the mining process. The sulfide minerals react with oxygen in air or pore water and produce sulfuric acid. Acid rock drainage is thus low-pH water with elevated concentrations of iron, sulfate, and heavy metals and metalloids of varying composition dependant upon the originating mineral deposit type.

The purpose of this document is to identify passive and semi-active treatment technologies that could potentially be used at the Elizabeth Mine Site (herein after referred to as the Site), present general capital, operation and maintenance costs for specific treatment technologies, and discuss the relative success of these treatment technologies at other sites. Technologies reviewed are inclusive of the passive treatment methods of aerobic wetlands, anoxic limestone drains (ALD), open limestone channels (OLC), settling ponds, successive alkalinity-producing systems (SAPS), and solid-reactant anaerobic sulfate-reducing bacteria (SRB) bioreactors, and the semi-active method of liquid-reactant SRB bioreactors.

1.1 LIMITATIONS OF AVAILABLE INFORMATION

The evaluation of passive treatment systems has involved numerous discussions with system designers and operators. Numerous examples of failed systems have been identified. In the majority of these cases, evaluations to determine how and why systems failed were not generally performed, or this information was not otherwise made available to URS. It was found that the owners were unwilling to invest additional money to evaluate the failure cause without financial benefit. Therefore, detailed information on system failures is somewhat limited.

Additionally, as many treatment technology applications have been research-based, for proprietary reasons developers have been guarded in discussing details of either processes or applications with URS.

This section describes the generalized history of passive treatment systems and currently available passive treatment system components.

The overview is based on application experience combined with information provided by several well-known experts in the field, an extensive literature search, and review of recent technical publications. Appendix A presents a bibliography of reviewed publications, arranged by topic. Appendix B includes several overview papers useful in defining the technologies and applications history. Significant recent publications outlining case studies of individual applications are included as Appendices C, D, and E. Information provided and case studies reviewed include those associated with publicly available records. Information on systems developed and/or operating under confidentiality agreements are not included.

2.1 PASSIVE TREATMENT HISTORY

The cost of potentially perpetual treatment of ARD using traditional active lime treatment technology has caused the mining and regulatory communities to search for less expensive alternative treatment solutions. In the late 1970s and early 1980s, evidence from coal mine drainages suggested that wetlands, with their complex mix of biological, chemical, and physical processes, could potentially treat ARD. In the 1980s, the use of constructed wetlands was attempted to mimic natural wetlands and treat ARD.

Researchers developed hypotheses as to which wetland processes (e.g., plant uptake, adsorption, microbial reactions) were most important in the treatment of ARD. Early research in the field of passive wetland treatment focused on maximizing these processes. In the late 1980s and early 1990s, a practical understanding of the biological and chemical processes was developed and several authors (i.e., Brodie 1992; and Hedin, Nairn, and Kleinmann 1994) published guidelines for designing treatment systems (e.g., aerobic constructed wetlands) based on the influent water chemistry (Figure 1).

In one early investigation of a treatment wetland (Brodie 1992), ARD emanating from the base of a coal debris pond flowed under an old roadbed made of limestone rubble. The limestone from the roadbed was found to add alkalinity to the anoxic subsurface flow, which in turn allowed iron to precipitate when it became oxidized in the adjacent wetland. From this research originated the ALD concept. Open limestone channels were also used to add alkalinity to ARD before it enters a constructed wetland.

Much of the early work focused on passive treatment of ARD at eastern U.S. coal mine sites. These techniques were then applied to hard-rock drainages. Investigators found that typical hard-rock ARD had lower pH (i.e., <4) and higher concentrations of heavy metals (e.g., copper, zinc) that could not be treated as effectively with aerobic surface-flow constructed wetlands (Day, Filipek, and Papp 1986). In response, researchers attempted to employ subsurface processes of natural wetlands, mainly bacterially mediated anaerobic sulfate reduction systems (e.g., SRB systems). The sulfide produced by this process was found to bind with iron and most heavy metals, re-forming the same minerals that had originally been mined. Constructed wetlands designed to form metal sulfides are referred to as SRB constructed wetlands.

To maximize the subsurface processes, the ARD flow was discharged through an organic substrate that typically had relatively low permeability. The treatment processes that remove the

metals tended to further decrease the permeability during operation. Finally, researchers found that anaerobic systems typically function better without vegetation and when they are covered.

Current anaerobic system designs typically include pipes, valves, back-flush mechanisms, and other engineered features not found in natural wetlands. Thus, the anaerobic systems have evolved into designed systems that attempt to mimic natural geochemistry. These systems are better termed anaerobic bioreactors than anaerobic constructed wetlands because their design must counter physical and biological processes that occur naturally in wetlands.

The advancement of ARD treatment technologies for hard rock drainage has occurred in conjunction with advances in coal mine drainage treatment methods. For example, the SAPS used to treat components of ARD is a variant of the anaerobic bioreactor developed for coal mine drainage. Kepler and McCleary (1994) first reported using this concept to solve the problem of precipitation of iron hydroxide minerals and concomitant clogging in ALDs whenever the influent ARD was oxygenated and had high concentrations of iron. The goals of a SAPS design are to remove oxygen and reduce Fe^{+3} to Fe^{+2} , but not necessarily to precipitate metal sulfides. Thus, there is no attempt to maximize SRB processes.

To overcome the permeability issues typically associated with anaerobic bioreactors, some designers have added liquid organic reactants, such as alcohol to the treatment process, rather than the compost, wood chips, sawdust, or similar solid organic reactants used in most anaerobic bioreactors as documented by Tsukamoto and Miller. Such systems are referred to in this text as semi-active technologies.

The benefit of these systems is they can be relatively low maintenance, perhaps as low as the solid-reactant systems. In a variant of this method, a small plant can be built to co-treat ARD with a local processing waste or the liquid in sewage so that the two waste streams essentially treat each other. To the best of our knowledge, to date only one such co-treatment pilot system has been built (i.e., Jerome, Arizona) as documented by Allbright (2002).

During the past 20 years since research in passive and semi-active treatment methods began, researchers have gained a better understanding and respect for the complex interaction of the myriad of biological, chemical, and physical processes involved in the formation and treatment of ARD. The flow chart presented in Figure 1 shows an example approach to selecting a functional passive system. The concept of passive treatment has been tempered by experience. To date there has been no successful application of a completely passive method that effectively treats the typically less benign ARD from heavy metal mining. This review has found that all constructed systems to date have required some level of ongoing maintenance and periodic reconditioning (reconstruction) and few are currently in operation.

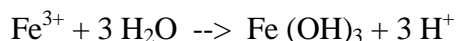
2.2 CURRENTLY AVAILABLE PASSIVE TREATMENT COMPONENTS

The following section summarizes the state of the practice of each of the common methods of passive and semi-active ARD treatment including aerobic wetlands, ALDs, OLCs, solid-reactant SRB anaerobic bioreactors, SAPS, and liquid-reactant SRB anaerobic bioreactors. To address specific issues relevant to Elizabeth Mine, the discussion focuses on solid- and liquid-reactant anaerobic bioreactors used to treat ARD.

2.2.1 Aerobic Wetlands

Aerobic wetlands and subaerobic wetlands are similar to natural wetlands in that the water flows mainly over the substrate surface. This type of wetland is well understood because it has a relatively long application history in municipal sewage treatment systems. Aerobic wetlands are typically shallow excavations filled with one to three feet of soil, gravel, and/or rocks in a hummocky pattern. The designed hummocks allow for variations in water depth of between one inch to approximately one foot to form a diversity of microenvironments. In these microenvironments, consortia of micro- and macro-organisms carry out a wide variety of biogeochemical processes.

The dominant processes treating mine drainage in the deeper portions of aerobic wetlands are oxidation of Fe^{+2} to Fe^{+3} by aeration spillways, precipitation of Fe^{+3} hydroxides, and settling of the hydroxides in settling ponds. Plants are typically used within the system because they help trap suspended matter and provide additional oxygen. Aerobic wetlands require sufficient alkalinity in the water to keep the pH from falling as a result of the hydrolysis of iron, following the reaction:



Through trial and error, a number of investigators have concluded that a system consisting only of aerobic wetlands is effective only in treating relatively benign ARD (e.g., pH >4.5, significant alkalinity, and relatively low heavy metal content). However, aerobic wetlands are often included as a final process step in a treatment system containing one or more other passive treatment methods, such as ALDs, OLCs, and/or anaerobic bioreactors. When used with ALDs or OLCs, aerobic wetlands act as oxidation and settling ponds. They are also typically used as polishing cells for effluent from SRB bioreactors to remove the nitrogen and organic breakdown products solubilized during SRB treatment. Aerobic wetlands have been used successfully to treat manganese, as discussed below.

Manganese Treatment by Aerobic Wetlands

Nearly all manganese will pass through ALDs, OLCs, and SRB bioreactors because manganese does not readily form manganese sulfides and, without catalysts, manganese requires a pH greater than 9 to precipitate. The dominant manganese removal processes are oxidation of Mn^{+2} to Mn^{+4} , precipitation of Mn^{+4} oxides, and settling of the oxides in settling ponds as a final polishing step after treatment for removal of acidity and all other metals.

Treatment of manganese requires a special type of aerobic wetland that is highly oxidizing and contains populations of microorganisms that help catalyze the precipitation reaction by locally raising the pH to between 8 and 9. To achieve these conditions, an aeration spillway typically precedes the wetlands to ensure that the water is highly oxidized.

Manganese wetlands are typically shallow rock wetlands colonized with an algal mat of green algae and cyanobacteria designed to locally raise pH and the oxidation-reduction potential (Eh) (Wildeman et al. 1993). A wetland without the appropriate algae and bacteria must be approximately five times as large as one with such a mat in order to achieve similar levels of effectiveness.

Adsorption and/or coprecipitation of heavy metals onto iron or manganese oxide minerals is a function of pH. The higher the pH, within the range of natural stream environments, the greater the adsorption (Filipek, Nordstrom, and Ficklin 1987). If the wetland is able to precipitate manganese, it will also be capable of significant removal of certain heavy metals, including copper, lead, and zinc (Filipek, Chao, and Carpenter 1981).

Proprietary methods for designing and constructing mixed microbial mats to treat manganese and other heavy metals are available through developers such as Microbial Aquatic Treatment Systems, Inc. Refer to Appendix C for information on this technology. However, applications experience has shown that similar results can typically be obtained by inoculating a wetland with sufficient matting (i.e., 5 to 10 percent of the wetland area) or by inoculating a shallow rock wetland with a naturally occurring consortium of green algae and cyanobacteria.

The process of obtaining a consortium of algae and bacteria acclimated to site conditions can be as simple as placing hay bales in a stream near the site in spring or summer and allowing the growth of green bacteria and algae to develop on the hay, which then can be dispersed into the constructed wetland as inoculum. Inoculating is effective because the algae and bacteria tend to “self-organize” to form and maintain their appropriate micro environments and the process can be achieved at a significantly reduced cost compared to the proprietary mats.

2.2.2 Anoxic Limestone Drains

An ALD is a trench filled with crushed high-calcium limestone, sealed with geotextile or plastic, and covered with clay or soil to prevent oxygen inflow (Figure 2). It is typically built into a hillside or tailing pile to capture ARD that has not yet been exposed to oxygen. As the acidic water flows through the ALD, the acid dissolves some of the limestone, which adds alkalinity to the water and raises the pH.

The US Bureau of Mines (Hedin, Nairn, and Kleinmann 1994) has produced guidelines for ALD design. These guidelines include: 1) the limestone should have at least 80-percent CaCO_3 content as the calcium-rich limestone is significantly more reactive than magnesium-rich limestone; 2) the limestone should consist of Nos. 3- or 4-sized materials (e.g., baseball-size) to minimize compaction and permeability decrease with time; 3) the limestone should be buried beneath several feet of clay, with heavy plastic separating the clay and limestone to limit oxygen infiltration; 4) the limestone should be inundated at all times; and, 5) to ensure limestone dissolution, the ALD is to be sized to provide a minimum retention time of 14 hours.

According to Hedin et al., a 14-hour retention time requires approximately 3000 kilograms (kg) of calcium carbonate for each liter per minute (l/min) of flow, regardless of water chemistry. These guidelines for designing an ALD have not changed significantly since published in 1994.

A properly designed ALD can raise the alkalinity of water flowing through it to about 200 milligrams per liter (mg/L) CaCO_3 equivalent. The guidelines for ALDs (Figure 1) indicate that they are most functional if the influent has the following characteristics:

- Dissolved oxygen (DO) <2 mg/L, oxidized Fe^{+3} <10 percent of the total iron, and
- Aluminum is <25 mg/L in the initial drainage.

Iron (III) and aluminum will precipitate on and coat, or armor, the limestone. The coating and aluminum floc will significantly reduce the limestone’s reactivity and the permeability of the

system, especially in low-flow conditions. Similarly, high concentrations of sulfate (i.e., > 1,500 mg/l) in acid rock drainage can cause precipitation of gypsum as the limestone dissolves, which will also reduce permeability (Nairn, Hedin, and Watzlaf 1991).

2.2.3 Open Limestone Channels

The OLC is a variant of the ALD and is used to treat discharges that are oxygenated and contain Fe^{+3} or high aluminum content. The OLC can be effective in adding alkalinity to ARD and raising the pH. However, OLCs require an environment that will self-scour the exposed limestone surface.

Ziemkiewicz et al. (1997) found that armored limestone in a turbulent stream was 50- to 90-percent as effective as unarmored limestone in neutralizing acid. The highest neutralization rates were associated with channels having slopes of between 45- and 60-percent, but some neutralization occurred on slopes as gentle as 8-percent. Accordingly, if sufficient topographic relief is present, an OLC is significantly more cost effective, is more easily monitored, and is more likely to be effective than an ALD for oxidized, aluminum-rich waters.

Design of an OLC must have a significant vertical gradient to allow for turbulent flow to strip off precipitates and must contain a number of small ponding areas between turbulent points to collect the resultant precipitates. Sizing considerations are similar to those for an ALD, except that typically a 50-percent efficiency should be assumed for yearly dissolution tonnages to account for potential armoring.

2.2.4 Settling Ponds

Settling ponds are used to collect treated or partially treated waters discharging from an ALD or OLC. These ponds allow iron and other precipitates to settle and are useful in providing a more constant flow rate into a downgradient treatment cell (e.g., SRB bioreactor). Settling ponds should be sized to allow a retention time of approximately 14 days.

Upon emerging from an ALD, water with reduced Fe^{+2} must be oxygenated in the atmosphere to allow oxidation of the iron and precipitation of iron oxyhydroxides such as ferrihydrite. Oxygenation of the water can be most simply accomplished by having it flow over a series of riffles before it enters a pond. At common temperatures, oxygen is soluble in water to approximately 8 mg/L. Stoichiometrically, 8 mg/L of oxygen can oxidize approximately 50 mg/L of Fe^{+2} . Therefore, each settling pond can only remove approximately 50 mg/L of initially reduced iron unless it is equipped with an active aeration device to add oxygen directly into the settling pond. To achieve this aeration by passive means, the site must have sufficient topographic relief and area to allow for a number of small settling ponds in series, each at a lower elevation than the previous. Passive oxygenating structures such as riffles are then placed in between each pond.

2.2.5 Successive Alkalinity Producing System (SAPS)

The goal of a SAPS is to add alkalinity to ARD and then precipitate iron hydroxides upon subsequent oxygenation using two separate steps to limit iron hydroxides from armoring the limestone. A SAPS is a variant of the anaerobic systems used mainly to treat coal mine drainage. Successive Alkalinity Producing Systems can be designed specifically for those

instances that are not appropriate for ALDs (i.e., waters with DO concentrations greater than 5 mg/L and high concentrations of oxidized Fe^{+3}).

Zipper and Jagie (2001) developed guidelines for the design and construction of SAPS (Appendix B). The SAPS uses ponded water above a 2-layer solid system of organic material overlying limestone (Figure 3). The hydraulic head differential achieved by the ponded water forces flow downward through the organic material to remove oxygen from the water and reduce iron. The reduced water then flows through the limestone and receives alkalinity without immediate precipitation of iron hydroxides. Once the water has obtained alkalinity from the SAPS, it flows into a settling pond where it becomes re-oxidized and iron hydroxides precipitate and settle out.

This system uses a much thinner layer of organic substrate than the SRB anaerobic bioreactor, but still suffers from progressive reduction in permeability and short-circuiting. Based on Demchak, Skousen, and Morrow (undated), the SAPS designed to date have been unable to eliminate the short-circuiting that lower their effectiveness in removing copper and zinc as sulfides. Demchak et al. recommend that several treatment cells be developed in series to combat this problem.

2.2.6 Solid-Reactant Anaerobic or Sulfate Reducing Bacteria (SRB) Bioreactors

The chemical processes in anaerobic bioreactors are bacterial oxidation of organic matter with concomitant reduction of DO, ferric iron (Fe^{+3}), and sulfate. Because sulfate-reducing bacteria (SRB) play a major role in this type of bioreactor, the anaerobic bioreactor is often called an SRB bioreactor. As sulfate reduction occurs, the produced sulfide then reacts with iron, copper, zinc, and cadmium to form metal sulfides. Metal sulfide production is the only effective passive means of reducing copper, zinc, and cadmium concentrations in ARD.

Reduction occurs in the absence of oxygen, which requires that flow be uni-directional and preferably vertical throughout the organic bioreactor material (i.e., substrate) within the subsurface. Uniform flow rates and even flow distribution through the substrate are critical in effective SRB bioreactor treatment. Accordingly, the bioreactor must be appropriately engineered to maximize vertical flow and, as with SAPS, to minimize short-circuiting.

The organic material substrates typically used in a solid-reactant SRB bioreactor contain a complex mixture of organic compounds, each serving as an energy source for a particular group of bacteria or fungus. Thus, an effective SRB bioreactor must contain microenvironments that allow an entire consortium of microorganisms to prosper (i.e., provide a good energy source for the SRBs and provide for sufficient alkalinity). For SRB bioreactors, a pH of about 5.5 or higher is preferred.

First-generation bioreactors typically used composted cow manure or mushroom compost because they provide significant alkalinity (Filipek et al. 1992; Schafer and Filipek 1995). More recent bioreactors use a combination of limestone, sawdust and alfalfa hay in place of manure because this combination 1) provides alkalinity; 2) provides significantly greater permeability; and, 3) appears to be a better energy source for the bacterial community. Cow manure is typically added only in small quantities as an inoculum to supply an initial source of active SRBs.

The design of a solid-reactant SRB anaerobic bioreactor consists of a lined basin containing the solid organic substrate. In the most effective designs, the substrate is typically sandwiched between pipes set in inert gravel near the top and bottom of the basin (Figure 4). The ARD flows into the bioreactor through one set of pipes and the treated water flows out through the other.

When inflow is through the reactor top, the system is in “downflow” mode. When inflow is through the reactor bottom, the system is in “upflow” mode. The more successful designs allow the flow to be reversed between modes.

Plugging of valves can occur due to the formation of precipitates if the chemical environment changes in the vicinity of the pipes. Precipitation of iron and aluminum hydroxides was a major problem in early SRB bioreactors because the pipes were sometimes laid in a bed of limestone. The limestone raised the pH and caused the same clogging as occurs in ALDs treating water with high concentrations of Fe^{+3} and/or aluminum. Recent systems incorporate pipe valves that allow them to be flushed out periodically to remove precipitates.

On start-up of the SRB bioreactor, the soluble organic compounds are especially prevalent, usually giving the effluent a brownish color. Also, the bacterial population needs time (i.e., two or three months) to become established in the bioreactor. Ideally, only a portion of the total effluent load is allowed to enter the bioreactor during this time period. Recirculating some of the treated effluent back into the reactor makes up the remainder of the flow. Due to the reactions in SRB bioreactors, soluble organic and nitrogen compounds, as well as sulfides, are produced. These compounds must be removed from the effluent before release off-site. Typically, this is accomplished by placing a small aerobic polishing cell in line after the SRB bioreactor.

The bioreactors were originally considered passive because they were believed to be able to function on the order of 20 or more years before requiring major maintenance (i.e., replacement of the treatment media). In the past 10 years a number of pilot SRB bioreactors have been used successfully over short periods to reduce heavy metals such as copper and zinc from sulfate-laden hard-rock drainage. However, none have remained operational for more than a few years without significant overhaul or modification. Between 3 and 4 years is the maximum reported operational period of an SRB bioreactor. Most systems were terminated for various reasons after a year or less. Identified causes of termination have included:

- Systems being overtaken by volunteer plants that added oxygen to the subsurface through their roots;
- Short-circuiting due to compaction and low permeability;
- Systems being overwhelmed by storm surges with acidity and metal loading significantly greater than design loads; and
- System desaturation.

Sizing of the organic portion of constructed SRB bioreactors is based on four primary criteria:

- Sulfate loading;
- Heavy metal loading;
- Residence time required for the sequence of bacterial reactions to occur; and
- Minimum vertical transport time allowed by the permeability of the substrate.

Sizing calculations must be conducted for each criteria to determine which is the limiting factor.

Sulfate Loading

Under optimum field conditions, sulfate reduction occurs at the rate of about 0.3 moles sulfate per cubic meter per day ($\text{mol}/\text{m}^3 \text{ day}$). Thus, the flux of sulfate into the system must be less than this rate. Sulfate loading is a very conservative factor because it assumes that the bacteria reduce all sulfate. Typically, sulfate concentrations do not drop below a few hundred milligrams per liter. The calculation is useful, however, because in order to function properly, the system requires that sulfate be present at levels in excess of metals.

Heavy Metal Loading

The flux of heavy metals, including iron, copper, lead, zinc, and cadmium, into the system must be less than the rate of sulfate reduction. Typically, a flux value of $0.15 \text{ mol}/\text{m}^3 \text{ day}$ heavy metal is used.

Residence Time

Metal sulfide precipitation requires at least 3 to 5 days to occur. Therefore, the bioreactor must be sized to allow a minimum of 3 days residence time within the unit. The porosity of the chosen substrate must be determined in order to evaluate residence time.

Permeability Constraints

An initial permeability of between 5×10^{-4} centimeters per second (cm/sec) and 1×10^{-5} cm/sec is common for the compost substrates used for the first generation of SRB bioreactors. When initial permeability was high it typically dropped rapidly following system start-up due to settling and compaction. Therefore, a value of no greater than 1×10^{-4} cm/sec should be assumed for compost substrates. The composted substrate in an SRB bioreactor should be at least 2 feet thick, but should not exceed about 3 to 4 feet in thickness because the substrate tends to compact with depth and can become too low for effective treatment. Additionally, short-circuiting due to preferential flow paths can develop when the permeability becomes too low relative to the pressure head of water in the system (Filipek et al. 1992; Cevaal and Whiting 1994).

The most recent generation of SRB bioreactors, such as that at the West Fork Unit of the Doe Run Mine use sawdust instead of compost for the majority of the organic substrate. This material has a significantly higher permeability, likely on the order of 10^{-2} cm/sec to 10^{-3} cm/sec . As with compost, it is also vulnerable to compaction, especially if heavy machinery is allowed to run over it during construction or maintenance. In general, it is believed that upflow reactors (i.e., systems which force water up through the contact media) tend to last longer than downflow systems because the upward flow tends to counter the tendency toward compaction and limit the resulting flow problems (e.g., development of preferential flow paths).

Flow Rate Variability

As evidenced in case studies, large flow variations can overwhelm anaerobic bioreactors if they are sized for lower flow rates. Conversely, if an SRB bioreactor is sized for maximum probable flow and the flow decreases significantly, some of the anaerobic substrate can become oxidized and release metals that had previously been precipitated. Release of metals is a potential problem especially in upflow bioreactors because the treated water will flush metals released during oxidation of the upper substrate as it leaves the bioreactor. If the flow and/or metal loading to the bioreactor increases significantly above the design flow, especially as in a spike increase event, the bacterial community in the bioreactor may suffer severe die-off and significantly reduce system effectiveness and require additional system maintenance (e.g., the microorganism consortium allowed to re-establish, the addition of new inoculum).

To accommodate flow variations into a system design, three options are typically used:

- Regulate flow to the bioreactor using a holding pond;
- Construct a series of bioreactor cells so that overflow from one cell can be treated in another; and
- Cover the top of the bioreactor cell(s) with a layer of geochemically inert gravel to accommodate head fluctuations due to flow variations.

Waste Generation

If it is required that spent substrate be removed from the site, the substrate should be discarded before concentrations of metals (e.g., cadmium, copper) become elevated and cause the substrate to fail leaching tests (i.e., toxicity characteristic leaching procedure [TCLP]) and be classified as a RCRA hazardous waste. To mitigate this potential cost the substrate should be tested periodically while the bioreactor is operating to monitor total metal concentrations and TCLP levels.

2.2.7 Liquid-Reactant (Semi-active) Bioreactors

SRB bioreactors suffer from three deficiencies that have recently been overcome by use of a liquid-reactant bioreactor. These deficiencies, and the corresponding effects of a liquid-reactant SRB, are as follows:

- 1) The solid reactant SRB bioreactor decreases in permeability with time because the organic reactant is also the physical matrix. As the matrix reacts, it breaks down into smaller pieces, the pore spaces decrease, and flow is restricted. In the liquid-reactant bioreactor, the matrix consists of nonreactive cobbles, which maintain a constant permeability over time as precipitated metals are removed through a filtration system.
- 2) The rate of the SRB reaction in the solid-reactant bioreactor cannot be controlled because the reactant substrate must be added in excess to allow for multi-year life. The sawdust and compost substrate in the bioreactor is a mix of several organic compounds. The SRB utilize only a subset of these compounds, each at a different rate. As the preferred SRB energy source becomes depleted, alternative compounds are used, but at a slower rate. Thus, the overall rate of sulfate reduction decreases with time. Also, as the temperature decreases from summer to winter, the reaction rate concurrently decreases.

By contrast, in the liquid-reactant bioreactor, an alcohol such as methanol, ethanol, or ethylene glycol (which are preferred energy sources for SRB) is added at a controlled rate based on the stoichiometric relation between the alcohol and the sulfate being reduced. Sodium hydroxide is also added to bring the pH to a level in which the SRB can thrive. The reaction rate can thus be better controlled.

- 3) In cold climates there is the possibility that the solid-reactant SRB bioreactor will freeze in the winter. The alcohol of the liquid-reactant bioreactor acts as an anti-freeze, keeping the bioreactor active and protecting the piping and valves.

These benefits of the liquid-reactant bioreactor can in some instances compensate for the added costs of operation and maintenance over a traditional SRB bioreactor.

Similar to the previous discussion on solid-reactant SRB bioreactors, sizing of the liquid reactant system is dependent on sulfate loading, metal loading, and residence time. However, in place of the permeability concerns inherent with the design of the solid-reactant system, liquid-reactant systems must also design around water acidity levels as well (Tsukamoto, undated).

Based on the available information, URS believes the liquid-reactant SRB bioreactor has significant potential for success. Experiences with bacterial water-treatment systems for sewage treatment applications, as well as experience with solid-reactant bioreactors could potentially supplement the success encountered in the field (see discussion below on Leviathan Mine research application) and lead to further applications of this technology.

The following are five short case histories excerpted from papers included in this report as Appendix D. The first case study is the Burleigh Tunnel SRB pilot cell designed by Camp Dresser McKee for the EPA and the Colorado Department of Public Health. It was one of the two longest continuously operated bioreactor systems identified during this review. The second, third, and fourth case studies presented are cells designed by Mr. Jim Gusek and coworkers at Knight Piesold and Co., who have designed some of the more long-lived and best-documented anaerobic bioreactors. The fifth case study presented is the Leviathan Mine site where Dr. Tsukamoto used a liquid-reactant SRB bioreactor to treat ARD.

The five case studies include the two longest operated SRB bioreactors for which information is available. Based on the literature review, no SRB bioreactor designed to treat ARD with heavy metals such as copper, zinc, or lead has operated more than 3½ or 4 years without either a decrease in substrate permeability or other problems resulting in significant reductions in treatment efficiency and either cessation of operation or system re-construction.

3.1 BURLEIGH TUNNEL PILOT CELLS

The Burleigh Tunnel site is at an elevation of 9,500 feet and has a long season of below-freezing temperatures. Two pilot SRB bioreactor cells, one upflow and one downflow, were designed to each treat 7 gpm of neutral-pH water with high zinc and cadmium concentrations draining from the Burleigh Tunnel in Colorado. The cells used first-generation bioreactor technology with a 4-foot deep substrate containing a mix of composted cow manure and wood chips with alfalfa hay, with a design permeability of 1.7×10^{-4} cm/sec. The cells were installed below grade to limit effects due to freezing. The upflow system was operated for 3 years, beginning in fall 1993. Flow to the downflow cell was discontinued in the third year due to permeability losses that blocked flow.

Both cells were effective in removing zinc during their first year of operation, when treating their design flow. During the 1995 spring runoff, the upflow cell was inundated with 20 gpm of lower-pH, higher-zinc aerobic water. This water appeared to have changed the microbial ecology of the bioreactor. The cell never recovered and, thereafter, was only 50- to 60-percent efficient in treating zinc.

3.2 BREWER PAD 5 PILOT CELL

According to Gusek (2000), the Brewer Pad 5 pilot cell treated ARD with elevated iron, aluminum, and copper concentrations from a spent heap leach pad from 1993 through early 1995, after which time it was decommissioned. The cell was 2.4 feet deep and filled with a mixture of composted turkey manure, sawdust, phosphate rock reject (limestone), and cow manure SRB inoculum. Influent metal concentrations increased significantly over the design concentrations (e.g., iron by over an order of magnitude) throughout the life of the bioreactor. Therefore, the influent flow was gradually decreased from the design value of 5 gpm to 0.75 gpm by the end of cell's life.

During its 18 months of operation, the cell suffered three episodes of invasion by volunteer vegetation at the cell surface. The vegetation caused oxidizing conditions within the cell which made the cell ineffective for copper removal. When the vegetation was eliminated and the cell refitted with a fresh source of native hay, the cell was able to remove iron, aluminum, and copper

with nearly 100-percent efficiency. Following the vegetation removal, the bioreactor was able to treat the increasingly concentrated but lower-flow rate ARD for the approximate three months until the system was decommissioned in early 1995 to accommodate ongoing reclamation/closure activities at the site (Gusek, 2000).

3.3 FERRIS-HAGGERTY MINE/OSCEOLA TUNNEL

The Ferris-Haggerty Mine/Osceola Tunnel site is a high-elevation abandoned copper-mine site with ARD characterized initially as having neutral pH, low sulfate, elevated copper concentrations, and water temperature close to freezing. A pilot cell treated a flow of 3 to 5 gpm for two years beginning in the summer of 1997. The cell was enclosed in a shed to aid in water sampling during high-snowfall months. The 4-foot deep cell was filled with a mixture of softwood sawdust, hay, limestone, cow manure, and gypsum. The gypsum was added as a source of sulfate for the SRB.

During operation, copper removal efficiencies were acceptable even when the cell surface was 40-percent covered in ice and the influent changed to an acidic water with a pH between 3.5 and 4. The pilot cell operated successfully (i.e., 89- to 97-percent removal of copper) for two years, after which time it was decommissioned. In 1999, a second pilot-scale cell was built with a slightly different substrate mixture and buried below grade to more closely mimic the planned full-scale system (Gusek 2000). Data are not available for the second pilot scale cell, and no information is available regarding the implementation schedule for the full-scale system.

3.4 DOE RUN MINE

The two longest-running bioreactors are at the West Fork Unit of the Doe Run Mine site. They were designed to treat 1,200 gpm of pH 8 water containing elevated lead concentrations. The system, which included a 0.75-acre settling pond, two SRB cells (each of cell covering just under 1-acre), a 1.4-acre aerobic rock filter, and a 2.0-acre aeration pond. The system took about 4 months to construct. Each of the SRB cells has a substrate composed of approximately 60- to 70-percent sawdust, 20-percent limestone, and the remainder aged cow manure and alfalfa hay cubes. The cell permeability is significantly greater than the first-generation SRB bioreactors composed mainly of compost and is estimated to be significantly less than the design permeability of 5×10^{-1} cm/sec.

The cells have been treating the mine drainage since 1996. During that time, the substrate in each cell has been removed and replaced twice. The first substrate removal was required to correct design changes that had not been previously tested. The distribution pipes had been connected to commonly shared layers of perforated high density polyethylene (HDPE) pipe and geonet materials sandwiched between layers of geofabric in an attempt to control sulfide production in hot weather by creating intentional short circuiting. In practice, the layered geotextiles appeared to trap hydrogen sulfide gas (H_2S), which caused gas build-up and permeability decreases in the cells. In June 1997, the substrate from the south anaerobic cell was excavated and the cell refilled without the geotextiles. The north cell was treated similarly in September 1997.

In the summer of 1998, some portions of the cells were intentionally by-passed to maintain lower sulfide concentrations. This mode of operation caused short-circuiting and plugging of the cells.

Also, changed operations within the mine resulted in the mine effluent water containing increasing concentrations of fine sediment, which tended to block flow within the cells. Therefore, the entire top 4 feet of substrate from the south cell was replaced in early 1999 with a new mixture containing more limestone than the original mix. In 2000, the same action was taken with the north cell. Since that time, the cells have received no special treatment during the summers and have operated without reported problems (Murphy 2002).

3.5 LEVIATHAN MINE

A liquid-reactant bioreactor was designed and constructed to treat ARD from an area of the Leviathan Mine site. This summary of the system is based on documentation included as Appendix E. The bioreactor system consists of 2 cells, which together were designed to treat up to 16 gpm of water with an average pH of 4, average iron concentration of 167 mg/l, and average concentrations of copper, nickel, and zinc on the order of 1 mg/l each. Each cell is 6 feet deep and contains approximately 1 foot of manure at the bottom. The remainder of cell one is filled with wood chips, while cell two is filled with 2- to 6-inch cobbles. Both cells were inoculated with an anaerobic horse manure culture. Influent ARD enters each cell at the surface, flows laterally across the cell, and eventually is collected in three loops of perforated pipe located at the cell bottom.

As a research application by the University of Nevada-Reno, methanol was added for the first 8 months of operation and then a mixture of methanol, ethanol, and ethylene glycol was added for the remainder of the experimental period. The application rates of the additives varied throughout the period, but were typically between 1 and 3 times the stoichiometric equivalent needed to reduce the sulfate in the influent solution. Initially, the inflow was kept below 0.8 gpm because the valves for inflow and outflow plugged frequently. At 8 months, a weir was added to control inflow, standpipes were added to control outflow, and the liquid organic mixture was changed. At 18 months, base was added and the flow increased from an average of about 0.4 gpm to an average of about 6.5 gpm, typically treating the entire flow of the source seep. For approximately the next 2 years, the bioreactor system operated effectively to remove nickel, copper, and zinc.

This section describes the geologic setting of the Elizabeth Mine site and the geochemical conditions as currently defined.

4.1 GEOLOGY AND MINE FEATURES

The Elizabeth Mine is located in the towns of South Strafford and Thetford, Vermont and is the largest mining complex of the Vermont Copper Belt. Elizabeth Mine has a long history of copper surface leaching operations and, in later years, milling of copper sulfide ore deposits. The ore deposit is characterized as a “besshi-type” massive sulfide with mineralization occurring as massive bands and disseminated sulfides. Pyrrhotite is a principal mineral in the deposit, with other minerals present including chalcopyrite, sphalerite, cubanite, and others.

Primary physical features at the site include two open cuts (north and south open cuts), two tailing impoundments referred to as Tailing Pile 1 and 2 (TP-1 and TP-2), and a leach pile referred to as Tailing Pile 3 (TP-3). TP-1 and TP-2 were generated as a waste product from on-site milling and floatation processes that occurred in the 1940s and 1950s and consist of approximately 35-acres of hydraulically deposited fine sand and silt mill tailing. The impoundments have a maximum thickness of about 100 feet and are underlain by either alluvium or fill.

TP-3 is irregularly shaped, side slope leach pile varying in thickness from several feet to tens of feet and covers approximately 12-acres. This historic side slope leach pile is comprised of a heterogeneous mixture of boulders, cobbles, gravels, sands, and silts consisting of leach ore, roasted ore, and spent ore.

4.2 GEOCHEMISTRY OF ACID ROCK DRAINAGE

The principal features at the site resulting in ARD include tailing piles TP-1 and TP-2 and a leach pile TP-3. Water discharging from TP-1, TP-2, and TP-3 is known to have a low pH and contains elevated metals due to the natural oxidization of the sulfides contained in the ore. This oxidizing process occurs when sulfide minerals are exposed to air and water and can be a natural phenomenon or the result of mining beneficiation activities. The discharges from TP-1, TP-2, and TP-3 exceed state and federal water quality standards.

At the Elizabeth Mine, the drainage from tailing piles TP-1, TP-2, and TP-3 demonstrate the wide range of water chemistries that can be classified as ARD. Discharges range from moderate pH, anoxic waters (with potential to acidify upon exposure to oxygen) with relatively low metal content associated with TP-1; to low-pH, highly oxidic waters rich in a number of heavy metals associated with TP-3. Based upon USGS sampling and testing of seeps performed in April and August 1998, the drainage composition and condition encountered at three discrete sample locations at the Elizabeth Mine is as follows.

Tailing Pile 1

The seeps draining TP-1 tend to be anoxic, with measured DO concentrations averaging 0.87 mg/L for the two sampling periods. The measured DO concentrations were higher in the summer than in the spring and varied between the seeps tested, with the sample from the northwest corner of TP-1 containing higher DO than the other seep locations. Similarly, the ratio

of reduced iron (Fe^{+2}) to total iron was relatively high in these samples, ranging from 0.44 to 1.00. Iron was the dominant heavy metal in these waters, with a total iron concentration of 453 mg/L. Dissolved aluminum concentrations averaged 0.19 mg/L; copper 0.011 mg/L; zinc 0.055 mg/L; and manganese 4.0 mg/L. The pH of these seeps averaged 5.9. However, the calculated acidity was relatively high at approximately 850 mg/L CaCO_3 equivalent due to significant acidity contribution from dissolved iron species.

Tailing Pile 2

The seep draining from TP-2 had a DO concentration of 7 mg/L, (near saturation). The ratio of reduced Fe^{+2} to total iron was 0.06 and the pH was 3.2; both parameters indicating oxidation of iron within this tailing pile. Due to the lower pH, heavy metal concentrations were higher in the TP-2 seep than those draining TP-1. The dissolved iron concentration was 1,000 mg/L; the dissolved aluminum concentration was 7.0 mg/L; copper 0.06 mg/L; zinc 1.4 mg/L; and manganese 7.3 mg/L. The acidity was calculated to be approximately 2,670 mg/L CaCO_3 equivalent.

Tailing Pile 3

The seeps from TP-3 had DO concentrations ranging from 7 to 9 mg/L (near saturation), ratios of reduced Fe^{+2} to total iron of 0.24, and pH of 2.2; all components being similar to TP-2 and indicating oxidation of iron to be occurring within the waste rock pile TP-3. Due to the lower pH and the type of rock in TP-3, heavy metal concentrations were the highest monitored on site. The dissolved aluminum concentration was 225 mg/L; copper 165 mg/L; zinc 35 mg/L; and manganese 5.2 mg/L. Iron was less dominant in these seeps, averaging 505 mg/L. The acidity was calculated to be approximately 2,500 mg/L CaCO_3 equivalent, lower than acidity measured in the TP-2 seep due to lower concentrations of aluminum and iron.

Aerobic wetlands, ALDs, OLCs, settling ponds, SAPS, and solid-/liquid-reactant SRB bioreactors have all been used to treat ARD, either independently or in combination. Each has been successful under limited circumstances with the degree of success dependent upon the chemistry of the water to be treated and site characteristics. In most cases of ARD treatment, effective treatment systems use several treatment technologies in series to address the differing components of ARD (e.g., pH, heavy metal concentrations) and minimize the problems associated with any one component (e.g., managing unsteady flow rates).

The most common applications employ 1) addition of alkalinity using an ALD, OLC, or semi-active lime or caustic addition; 2) oxidation and settling ponds to remove iron and aluminum; 3) SRB anaerobic bioreactors to remove heavy metals as sulfides; and, 4) a series of aerobic wetlands to remove manganese, organics and BOD accumulated from the anaerobic treatment technologies. Typically, iron and aluminum are the metals of highest concentration in ARD. Removing the iron before treatment in an SRB bioreactor (Step 3) significantly decreases the required size of the SRB bioreactor. Removing aluminum before treatment in an SRB bioreactor significantly decreases maintenance requirements of the SRB bioreactor. Heavy metal-laden ARD without significant iron or aluminum can be treated directly with an SRB bioreactor, omitting Step 3.

5.1 CONCEPTUAL DESIGN

The discharge from TP-1 and TP-3 will require treatment to remove the dissolved metals and raise the pH. Historically, active lime precipitation treatment has been successfully used to raise the pH and remove metals from similar ARD discharges. The exact treatment chain is specific to the site conditions and dependant on the type and concentration of dissolved metals (water quality) and flow quantity.

To optimize the treatment process and minimize cost, it is beneficial to have a constant source inflow with consistent water chemistry. Variation in flow can require large storage areas to provide constant flow to the treatment cells. Variation in chemistry may require additional treatment steps and/or cells, increasing the overall cost. Preliminary indications suggest that the water discharging from the TP-1 toe is generally constant and appears to have a relatively consistent water quality. Conversely, the discharge from TP-3 is variable in both quantity and geochemistry. Flow is dependent on runoff potential and seasonal precipitation events, while metals concentrations may be dependent on frequency of runoff events (i.e., frequency of flushing events).

TP-1 Drainage Treatment Requirements

The likely treatment system to treat ARD emanating from TP-1, based on the current state-of-the-practice, includes:

- 1) Anaerobic addition of alkalinity using an ALD, or semi-active lime or caustic addition;
- 2) Oxidation and settling ponds to remove iron and aluminum; and
- 3) Aerobic wetlands with an algal mat to remove manganese and small amounts of copper and zinc.

The actual treatment chain and resultant size of treatment components is dependent on further Site characterization, results of geochemical modeling and on-site pilot tests of systems. The actual size of the system and components will consider design constraints, site conditions, influent quantity and properties, and effluent discharge criteria.

The likely treatment system assumes, among other things, that treatment specific for heavy metals removal (e.g., copper, zinc) will not be required to meet discharge levels for TP-1 drainage.

TP-3 Drainage Treatment Requirements

The likely treatment system to treat ARD emanating from TP-3, based on the current state-of-the-practice, includes

- 1) Addition of alkalinity using an OLC or semi-active lime or caustic addition;
- 2) Oxidation and settling ponds to remove iron and aluminum;
- 3) Solid or liquid-reactant SRB bioreactor(s) to remove heavy metals as sulfides; and,
- 4) Aerobic wetlands with an algal mat to remove manganese, organics and BOD accumulated from the anaerobic treatment technologies.

Based on the Leviathan Mine applications, although still considered in experimental stages, a liquid-reactant SRB bioreactors may potentially be useful in overcoming some of the inherent problems with the traditional SRB bioreactor for the application at TP-3. Continued evolution of the technology, and incorporation of engineering principles obtained from experiences with anaerobic digesters for sewage treatment and solid-reactant SRB bioreactors should improve their functioning and efficiency significantly.

Although system designers reference 30-year substrate life spans, no SRB bioreactor designed to treat heavy-metal laden ARD has yet operated continuously for more than about three to four years without requiring a change of substrate. Based on existing case histories of SRB bioreactor applications, URS believes the design life of the systems should be considered not to exceed four to five years to appropriately design and accurately evaluate system costs.

As with the TP-1 system, the actual treatment chain and resultant size of treatment components is dependent on further Site characterization, geochemical modeling and pilot test results; and the final size of the system components will be based on design constraints, site conditions, influent quantity and properties, and effluent discharge criteria.

5.2 FEASIBILITY LEVEL COST ESTIMATE

Based on the TP-1 and TP-3 treatment systems outlined in the previous section, feasibility level cost estimates have been prepared to forecast anticipated expenditures for capital, and operation and maintenance. The estimates are based on available site information, URS experience with constructing and operating similar systems, and on information obtained from the literature review.

Literature-Based Cost Information

Limited cost information is available from other sites where systems are in place to treat hardrock ARD. For system components such as ALDs, OLCs, SAPS, and settling ponds, cost estimates vary widely between applications and no correlation can be drawn directly for the Elizabeth Mine site from application history at other sites. The actual costs are highly dependent on specific site conditions. Variables that control costs of these components include 1) the influent flow rate; 2) the influent acidity; and, for ALDs, OLCs, and SAPS, 3) material acquisition and transport costs (i.e., limestone).

The estimated cost for constructing an aerobic wetland is largely a function of the type of microbial mat used. URS estimates that construction costs for an unlined wetland using inoculated hay bales can range from \$30,000 to \$40,000 per acre. For comparison, a similar system designed using a proprietary microbial mat is estimated to cost more than \$500,000 per acre, based on vendor costs of \$12 per square foot.

Cost estimates for constructing and operating a solid-phase SRB bioreactor with polishing cell are presented by Gusek in his Design Example No. 1 (Gusek, 2002b). The design includes 1.7-acres of 3-foot deep SRB cells and 0.25-acres of polishing cell. He estimates a cost of between \$30,000 to \$50,000 to complete bench and pilot studies, and \$315,000 for final system design and construction.

Gusek estimates annualized operation and maintenance, laboratory analytical, and substrate replacement costs to be approximately \$24,000. The estimate is based on a 30-year operational life and includes a replacement cost of approximately \$110,000, or approximately \$65,000 per acre. If a four-year operational life (replacement period) is used, which is consistent with current field operability findings, the annualized operation and maintenance, laboratory, and substrate replacement costs would be approximately \$52,500, or \$40,000 per acre per year, bringing the total operation and maintenance costs to approximately \$105,000 annually per acre.

The treatment system installed at the West Fork Unit of the Doe Run Mine (a case study discussed in Section 3.4) includes a 0.75-acre settling pond, two SRB cells, a 1.4-acre aerobic rock filter, and a 2.0-acre aeration pond. Gusek estimated the system cost at approximately \$700,000, including engineering and permitting (Gusek et al. 2000). According to Gusek (2002), the rock filter and aeration pond required significant cutting and filling of the subgrade and required membrane liners, increasing construction costs to about twice what he suggests they should typically be. Based on information provided by Gusek (2002), URS estimates the actual construction cost of the SRB bioreactor portion of the system to be approximately \$200,000 per acre (excluding permitting), slightly more than the design example provided above (Gusek, 2002b).

Cost estimates for designing, constructing, and operating a liquid-substrate bioreactor were presented by Gusek (2002). The system included a 4-acre, 6-foot deep liquid-substrate bioreactor combined with a 9-acre aerobic polishing cell (allowing for manganese and BOD removal). The system cost was about \$1,360,000 for design and construction. Assuming that the aerobic cells cost about \$270,000 to construct, and design costs are 10-percent, the liquid-substrate bioreactor cost about \$950,000, or about \$240,000 per acre.

Conversely, Tsukamoto (2002) estimated that the cost to construct two liquid-reactant SRB bioreactor cells treating up to 16 gallons per minute at Leviathan mine (discussed in Section 3.5)

was about \$120,000. The alcohol and sodium hydroxide costs were approximately \$0.75 and \$0.22 per 1,000 gallons treated, respectively. For this system, reported operating material (i.e., chemical) costs were typically less than \$5,000 per year. According to Tsukamoto, after the initial frequent monitoring phase during acclimation, long-term monitoring frequency was reduced to approximately one to two times per month.

Elizabeth Mine Cost Estimate

Feasibility level cost estimates for the likely treatment systems for TP-1 and TP-3 (as outlined above) are presented in Table 1 (Capital Costs) and Table 2 (Operation and Maintenance Costs). The costs are based on URS' experience with the design of ARD treatment systems and on the information and case studies identified during the literature review. Implementation of the TP-1 and TP-3 systems will require additional data collection and further detailed design analyses. Capital costs and operation and maintenance costs for the TP-3 system are provided for both a solid-reactant and liquid-reactant SRB.

Capital costs, as described in Table 1, are estimated to be \$268,500 for the TP-1 system, \$1,452,400 for TP-3 with a solid-reactant SRB, and \$1,688,400 for TP-3 with a liquid-reactant SRB.

Total annual operation and maintenance costs, as described in Table 2, are estimated to be \$48,500 for TP-1, \$120,000 for TP-3 with a solid-reactant SRB, and \$132,000 for TP-3 with a liquid-reactant SRB.

These estimates assume, among other things, that algal mats can be created at the site. Included are costs for engineering and design, pilot testing, and construction oversight. Due to the preliminary nature of the estimates we have also included a contingency of 30 percent, which includes both design and reserve contingencies.

The operation and maintenance costs were developed by estimating the weekly labor required per year. We assumed that one technician and one laborer would be required for field activities. As noted, the operation and maintenance cost estimates include on-site sludge disposal, monitoring, analysis, and analytical testing, but not oversight or data interpretation. Component replacement costs (i.e., 5-year SRB replacement) are included in the estimate for the solid-phase reactant system. Liquid reagent costs are included in the estimates for the liquid-phase reactant system. Other assumptions incorporated into the estimate are provided on Table 2.

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Tables

**TABLE 1
FEASIBILITY LEVEL CAPITAL COST ESTIMATE
PASSIVE/SEMI-ACTIVE TREATMENT SYSTEM, TP-1 AND TP-3
ELIZABETH MINE, VERMONT**

Description	Approximate Area (Acres)	Cost	
TP-1 Treatment System			
Anoxic Limstone Drain	0.01	\$35,400	
Oxidizing Ponds	0.5	\$98,300	
Aerobic Wetlands (1)	0.24	\$8,500	
	TP-1 Subtotal	\$142,200	
Engineering and Design (10%)		\$14,200	
Pilot Testing (20%)		\$31,300	
Construction Oversight (10%)		\$18,800	
	Subtotal	\$206,500	
Contingency (30% of Subtotal)		\$62,000	
	Program Cost	\$268,500	
Description	Approximate Area (Acres)	Cost Solid-reactant	Cost (4) Liquid-reactant
TP-3 Treatment System			
Open Limstone Channel	0.5	\$28,000	\$28,000
Oxidizing Ponds	0.25	\$57,500	\$57,500
Anaerobic Bioreactor (2)	2.5 (3)	\$676,400	\$726,900 (5)
Aerobic Wetlands (1)	0.2	\$7,500	\$7,500
	TP-1 Subtotal	\$769,400	\$819,900
Engineering and Design (10% for solid, 20% for liquid)		\$76,900	\$164,000
Pilot Testing (20%)		\$169,300	\$196,800
Construction Oversight (10%)		\$101,600	\$118,100
	Subtotal	\$1,117,200	\$1,298,800
Contingency (30% of Subtotal)		\$335,200	\$389,600
	Program Cost	\$1,452,400	\$1,688,400

(1) Includes locally developed algal mat - increase treatment area to 0.6 acres if no algal mat is used

(2) Cost can vary from less than \$165,000/acre to over \$240,000 per acre depending on the design constraints, local site conditions, influent properties and effluent discharge criteria. Actual cost should be verified by pilot testing.

(3) Liquid reactant will reduce the area, increase the depth and increase the unit cost

(4) Shows only cost changes due to liquid bioreactor

(5) Assumes two reactant storage tanks and simple shed with electricity

TABLE 2
FEASIBILITY LEVEL OPERATION AND MAINTENANCE COST ESTIMATE
PASSIVE/SEMI-ACTIVE TREATMENT SYSTEM, TP-1 AND TP-3
ELIZABETH MINE, VERMONT

Work Items	Work Weeks /Year
TP-1 Passive Treatment System	
Clean Horizontal Drains	2
Maintain ALD	1
Clean Settling Ponds (1)	6
Maintain Aerobic Wetlands	2
Subtotal TP-1	11
 Annual Labor Cost	
One Technician	\$40 per hr \$ 17,600
One Laborer	\$25 per hr \$ 11,000
One Truck (Wet)	\$15 per hr \$ 6,600
Small tools and equipment	\$500 per mth for 2.5 mths \$ 1,300
Backhoe Rental (Wet)	\$20 per hr for 11 wks \$ 8,800
Subtotal	\$ 45,300
 Material Cost	
(Assume approximately 1% of labor)	\$ 300
 Annual Monitoring	
(Assume approximately 10% of labor)	\$ 2,900
Total (5)	\$ 48,500

TABLE 2
FEASIBILITY LEVEL OPERATION AND MAINTENANCE COST ESTIMATE
PASSIVE/SEMI-ACTIVE TREATMENT SYSTEM, TP-1 AND TP-3
ELIZABETH MINE, VERMONT

Work Items	Work Weeks /Year		
	Solid-react(3)	Liquid-react	
TP-3 Passive Treatment System			
Maintain OLC	3	3	
Clean Settling Ponds (1)	4	4	
Maintain Anaerobic Bioreactor (2)	4	12	
Maintain Aerobic Wetlands	2	2	
Subtotal TP-3	13	21	
 Annual Labor Cost			
One Technician	\$40 per hr	\$ 20,800	\$ 33,600
One Laborer	\$25 per hr	\$ 13,000	\$ 21,000
One Truck (Wet)	\$15 per hr	\$ 7,800	\$ 12,600
Small tools and equipment	\$500 per mth for 3 mths	\$ 1,500	
Small tools and equipment	\$500 per mth for 5 mths		\$ 2,500
Backhoe Rental (Wet)	\$20 per hr for 21 wks	\$ 16,800	
Backhoe Rental (Wet)	\$20 per hr for 13 wks		\$ 10,400
Subtotal		\$ 59,900	\$ 80,100
 Material Cost			
Solid-reactant substrate replacement	\$ 55,000		(3)
Liquid-reactant ethanol and NaOH		\$ 43,700	(4)
 Annual Monitoring			
(Assume approximately 15% of labor)	\$ 5,100	\$ 8,200	
Total (5)		\$ 120,000	\$ 132,000

(1) Cost includes on-site sludge disposal

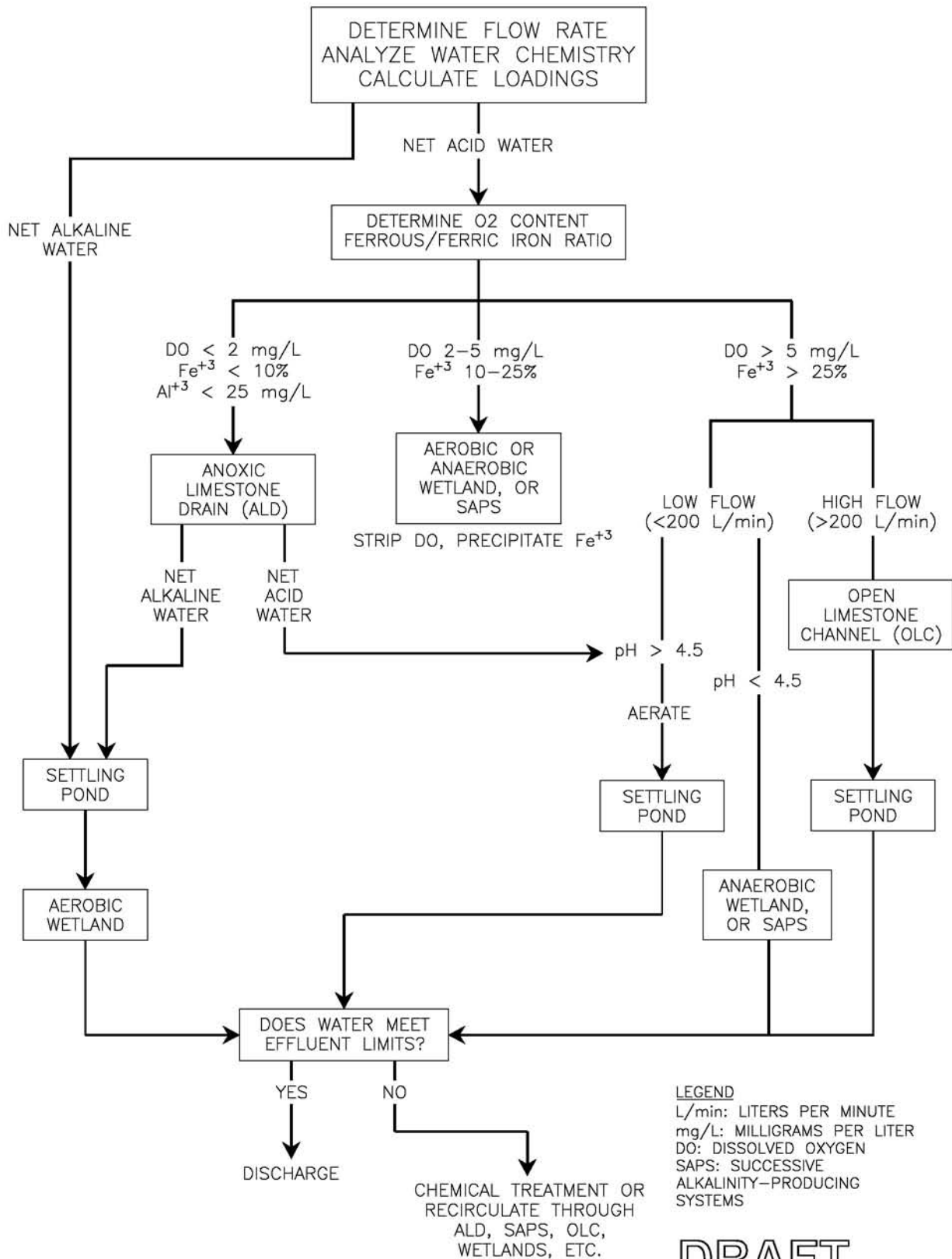
(2) Assumes flushing, monitoring, and addition/replacement of substrate.

(3) Assumes replacement of solid substrate every 5 years. @ half original reactor cost of \$676K.

(4) Assumes 2 times stoichiometric ratio for ethanol and Tsukamoto's base reagent costs for ethanol and NaOH. (Est. 1000 gal ethanol needed per week for TP-3.)

(5) Cost includes monitoring and analytical testing, but not oversight or data interpretation.

Figures



LEGEND
 L/min: LITERS PER MINUTE
 mg/L: MILLIGRAMS PER LITER
 DO: DISSOLVED OXYGEN
 SAPS: SUCCESSIVE ALKALINITY-PRODUCING SYSTEMS

DRAFT

NOTE:
 ADAPTED FROM HEDIN ET AL. 1994.

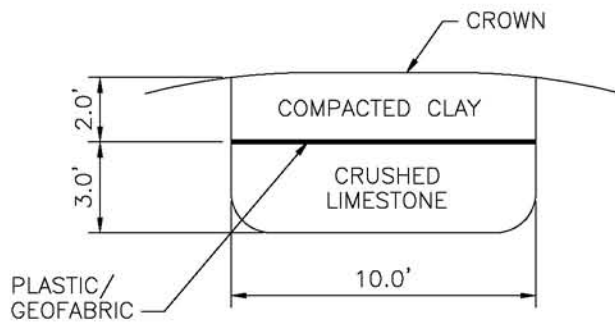
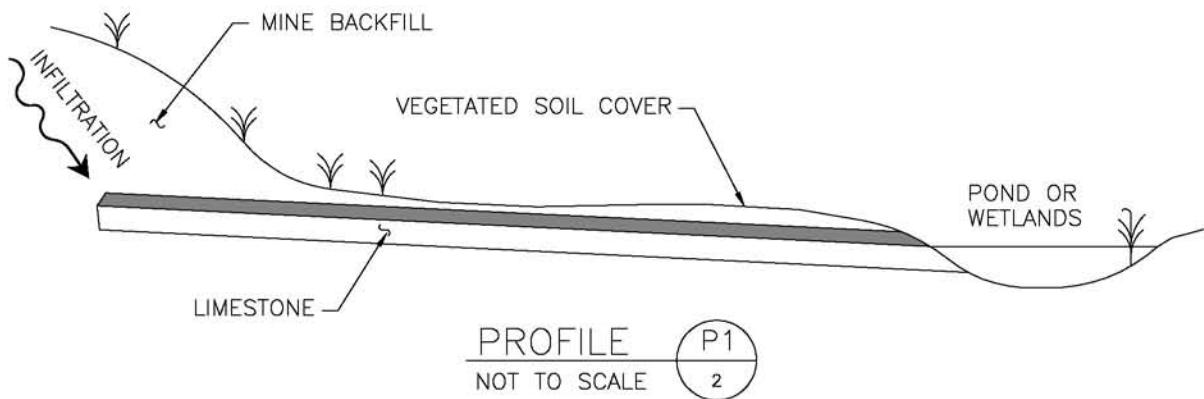
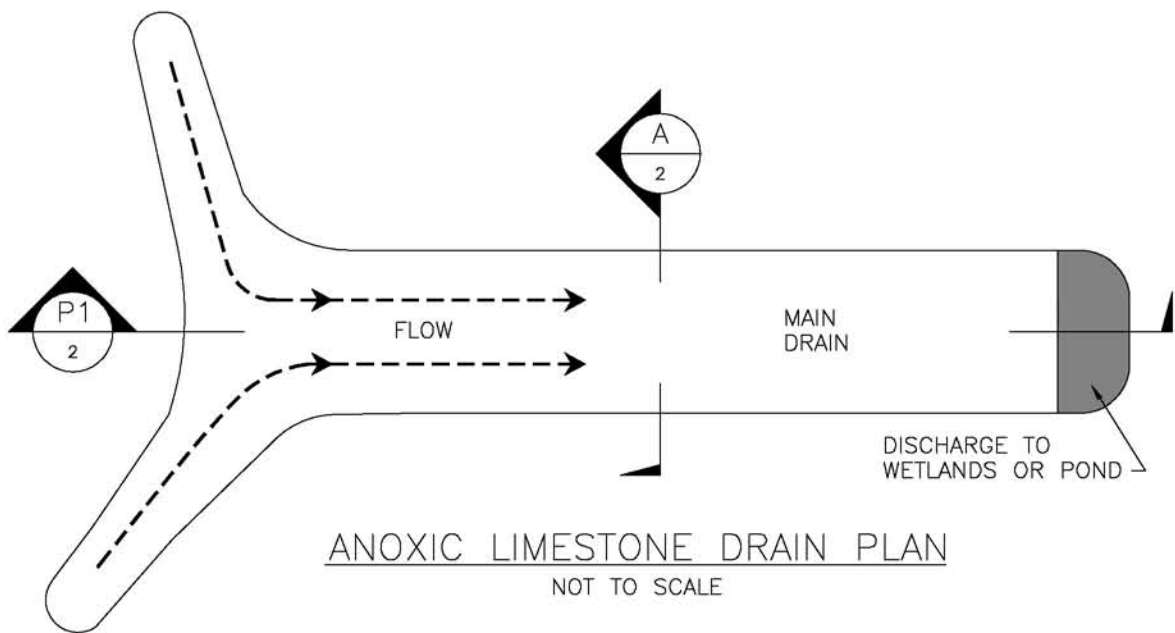


DESIGN: LF
 APPROVED: JCC
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 SCALE: NO SCALE
 DATE: 4-FEB-03
 FILE NO: AMD-FIGS1-4-FS

CLIENT: USAGE
 PROJECT: ELIZABETH MINE STRAFFORD, VERMONT

TITLE: FLOWCHART FOR SELECTING A PASSIVE ACID ROCK DRAINAGE TREATMENT SYSTEM BASED ON WATER CHEMISTRY AND FLOW

PROJECT NO: 13846-066
 DRAWING NO: 1



NOTE:
ADAPTED FROM BRODIE, 1992.

DRAFT

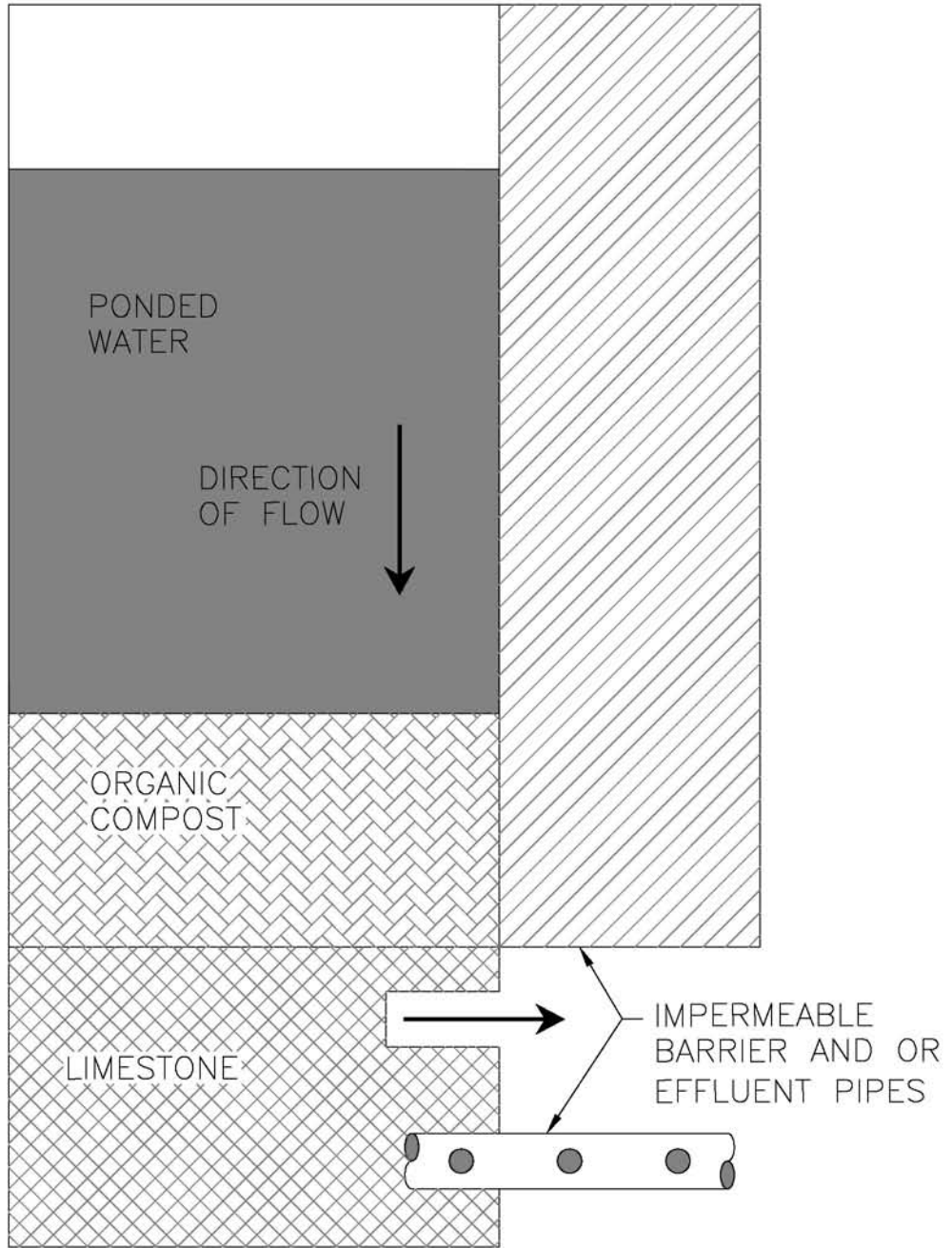


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SCALE: NO SCALE
DATE: 4-FEB-03
FILE NO: AMD-FIGS1-4-FS

CLIENT: USACE
PROJECT: ELIZABETH MINE STRAFFORD, VERMONT

TITLE: ANOXIC LIMESTONE DRAIN PLAN PROFILE AND SECTION

PROJECT NO: 13846-066
DRAWING NO.: 2



NOTE:
FROM KEPLER & MCCLEARY, 1994.

DRAFT

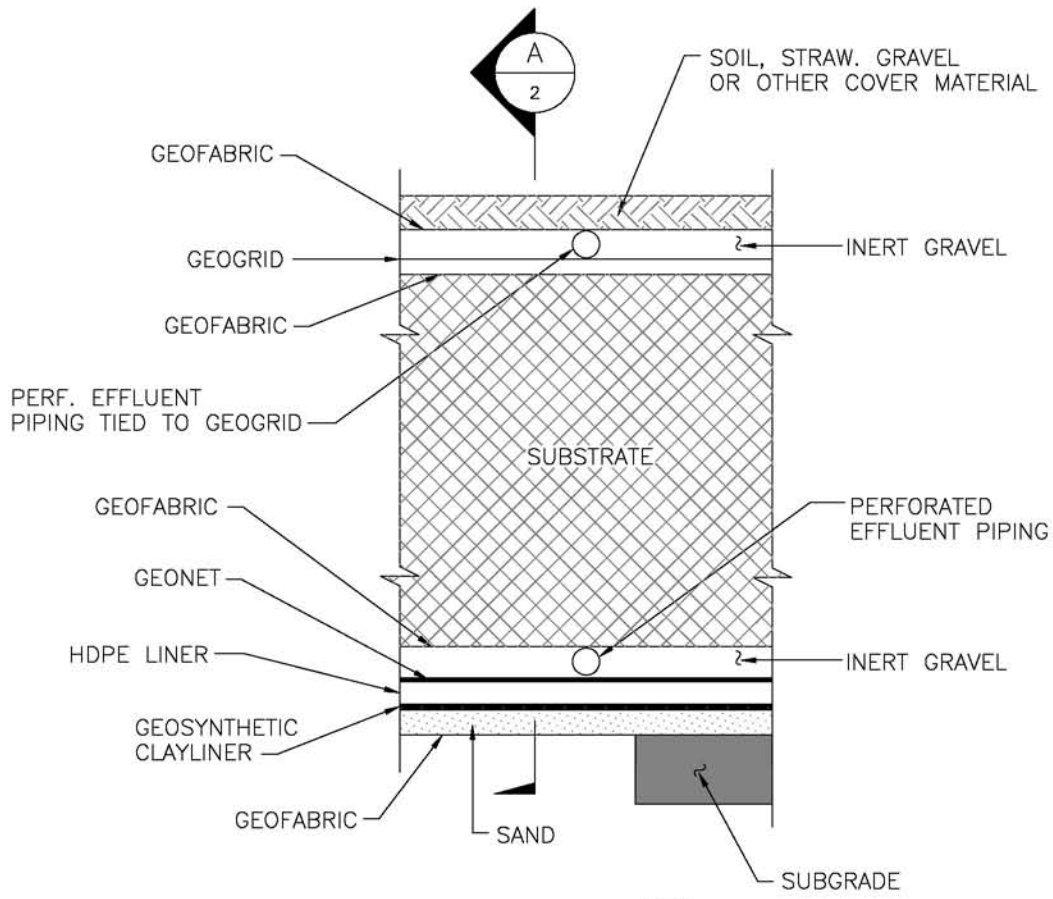


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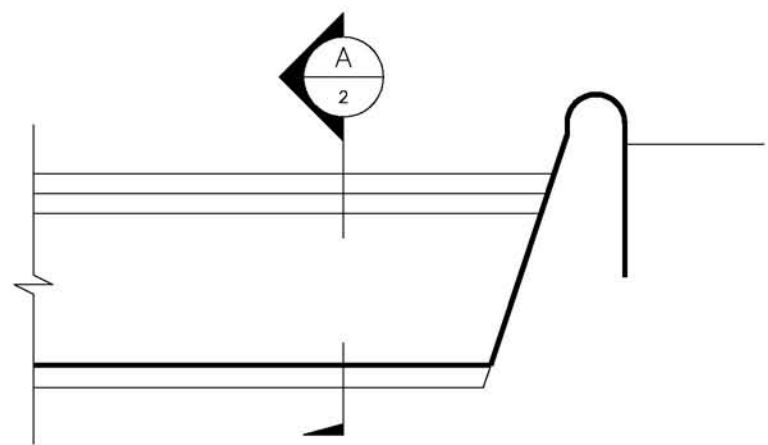
CLIENT: USACE
 PROJECT: ELIZABETH MINE
 STRAFFORD, VERMONT

TITLE: TYPICAL CROSS-SECTION VIEW OF A
 SUCCESSIVE ALKALINITY PRODUCING
 SYSTEM (SAPS) TREATMENT COMPONENT

PROJECT NO:
13846-066
 DRAWING NO.:
3



SECTION A
NOT TO SCALE 2



TYPICAL CROSS SECTION
NOT TO SCALE

DRAFT



DESIGN: LF
APPROVED: JCC
DRAWN: CNH
SCALE: NO SCALE
DATE: 4-FEB-03
FILE NO: AMD-FIGS1-4-FS

CLIENT: USACE
PROJECT: ELIZABETH MINE STRAFFORD, VERMONT

TITLE: SCHEMATIC CROSS SECTION OF UPFLOW AND DOWNFLOW SULFATE REDUCING BACTERIA ANAEROBIC BIOREACTOR

PROJECT NO: 13846-066
DRAWING NO.: 4

Appendix A
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Appendix B
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**Skousen
1998
Overview of Passive Systems for
Treating Acid Mine Drainage**

Overview of Passive Systems for Treating Acid Mine Drainage



Jeff Skousen
West Virginia University

Introduction

Active chemical treatment of AMD to remove metals and acidity is often an expensive, long term liability. In recent years, a variety of passive treatment systems have been developed that do not require continuous chemical inputs and that take advantage of naturally occurring chemical and biological processes to cleanse contaminated mine waters. The primary passive technologies (Figure 1) include constructed wetlands, anoxic limestone drains (ALD), successive alkalinity producing systems (SAPS), limestone ponds, and open limestone channels (OLC).


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Figure 1. Schematic diagram of passive treatment systems to treat AMD.

Natural wetlands are characterized by water-saturated soils or sediments with supporting vegetation adapted to reducing conditions in their rhizosphere. Constructed wetlands are man-made ecosystems that mimic their natural counterparts. Often they consist of shallow excavations filled with a flooded gravel, soil, and organic matter to support wetland plants, such as *Typha*, *Juncus*, and *Scirpus* sp. Treatment depends on dynamic biogeochemical interactions as contaminated water travels through the constructed wetland. ALDs are abiotic systems consisting of buried limestone cells that passively

generate bicarbonate alkalinity as anoxic water flows through. SAPS combine treatment concepts from both wetlands and ALDs. Oxygenated water is pre-treated by organic matter removing O_2 and Fe^{+3} , and then the anoxic water flows through an ALD at the base of the system. Limestone ponds are ponds built over the upwelling of a seep and the seep is covered with limestone for treatment. OLCs are surface channels or ditches filled with limestone. Armoring of the limestone with Fe hydroxides decreases limestone dissolution by 20 to 50%, so longer channels and more limestone is required for water treatment.

At their present stage of development, passive systems can be reliably implemented as a single permanent solution for many types of AMD and at a much lower cost than active treatment. Relative to chemical treatment, passive systems require longer retention times and greater space, provide less certain treatment efficiency, and are subject to failure in the long term. However, many passive systems have realized successful short-term implementation in the field and have substantially reduced water treatment costs at many mine sites (Faulkner and Skousen 1994). Current research seeks to understand the dynamically complex chemical and biological mechanisms that occur within passive systems and which are responsible for AMD treatment.

Selection of an appropriate passive system is based on water chemistry, flow rate and local topography and site characteristics (Hyman and Watzlaf 1995), and refinements in design are ongoing. Figure 2 (adapted from Hedin et al. 1994) summarizes current thinking on the appropriate type of passive system for various conditions. In general, aerobic wetlands can treat net alkaline water; ALDs can treat water of low Al, Fe^{3+} , and DO; and SAPS, anaerobic wetlands and OLCs can treat net acidic water with higher Al, Fe^{3+} , and DO. As scientists and practitioners improve treatment predictability and longevity of passive systems, they will be able to treat the more difficult waters of high acidity and high Al content.

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Figure 2. Flowchart for selecting a passive AMD treatment system based on water chemistry and flow (adapted from Hedin et al. 1994).

Natural Wetlands


Huntsman et al. (1978) and Wieder and Lang (1982) first noted amelioration of AMD following passage through naturally occurring *Sphagnum* bogs in Ohio and West Virginia. Studies by Brooks et al. (1985), Samuel et al. (1988), and Sencindiver and Bhumbla (1988) documented similar phenomena in *Typha* wetlands. Although evidence suggests that some wetland plants show long term adaptation to low pH and high metal concentrations, AMD eventually degrades the quality of natural wetlands, which is contrary to federal laws designed for wetland protection and enhancement. Such regulations do not govern use of artificially constructed wetlands for water treatment, leading to the suggestion that these engineered systems might provide low cost, low maintenance treatment of AMD (Kleinmann 1991). Over a thousand wetlands have since been constructed to receive AMD from both active mines and abandoned mine lands.


Constructed Wetlands

Mechanisms of metal retention within wetlands listed in their order of importance include: 1) formation and precipitation of metal hydroxides, 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. Other mechanisms include neutralization by carbonates, attachment to substrate materials, adsorption and exchange of metals onto algal mats, and microbial dissimilatory reduction of Fe hydroxides and sulfate.

The way in which a wetland is constructed ultimately affects how water treatment occurs. Two construction styles currently predominate: 1) "aerobic" wetlands consisting of *Typha* and other wetland vegetation planted in shallow (<30 cm), relatively impermeable sediments comprised of soil, clay or mine spoil, and 2) "anaerobic" wetlands consisting of *Typha* and other wetland vegetation planted into deep (>30 cm), permeable sediments comprised of soil, peat moss, spent mushroom compost, sawdust, straw/manure, hay bales, or a variety of other organic mixtures, which are often underlain or admixed with limestone. In aerobic wetlands, treatment is dominated by processes in the shallow surface layer. In anaerobic wetlands, treatment involves major interactions within the substrate.

Aerobic wetlands are generally used to collect water and provide residence time and aeration so metals in the water can precipitate (Pictures 1 and 2). The water in this case usually has net alkalinity. Iron and Mn precipitate as they oxidize, and the precipitates are retained in the wetland or downstream. Wetland species are planted in these systems for aesthetics and to add some organic matter. Wetland plants encourage more uniform flow and thus more effective wetland area.

 Image1.jpg (28063 bytes)

 Image2.jpg (33432 bytes)


Because of their extensive water surface and slow flow, aerobic wetlands promote metal oxidation and hydrolysis, thereby causing precipitation and physical retention of Fe, Al, and Mn hydroxides. The extent of metal removal depends on dissolved metal concentrations, dissolved oxygen content, pH and net alkalinity 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. Metal hydrolysis produces H^+ , but alkalinity in the water buffers the pH and allows metal precipitation to continue. Inorganic oxidation reaction rates decrease a hundred-fold with each unit drop in pH, but microbial oxidation may increase these. Following Fe oxidation, abiotic hydrolysis reactions precipitate Fe hydroxides. Therefore, aerobic wetlands are best used with water that contains net alkalinity to neutralize metal acidity. Abiotic Mn oxidation occurs at $pH > 8$ while microorganisms are thought to catalyze this reaction at $pH > 6$ (Wildeman et al. 1991).

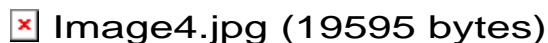
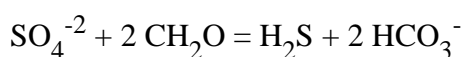
Manganese oxidation occurs more slowly than Fe and is sensitive to the presence of Fe^{2+} , which will prevent or reverse Mn oxidation. Consequently in aerobic net alkaline water, Fe and Mn precipitate sequentially, not simultaneously, with the practical result that Mn precipitation occurs (if at all) mainly in the later stages of wetland flow systems, after all Fe is precipitated.

Brodie and co-workers at the Tennessee Valley Authority (TVA) have reported extensively on their use of aerobic wetlands to treat AMD (Brodie 1993). A typical staged design might include an anoxic limestone drain (ALD, see next section) to passively add alkalinity to the source AMD, a settling basin to hold precipitated Fe flocs, followed by two or three aerobic wetland cells to sequentially remove additional Fe and Mn. Nine TVA wetlands receive moderate quality AMD (pH range of 4.1 to 6.3; total Fe <70 mg/L; total Mn <17 mg/L; total Al <30 mg/L; net alkalinity 35 to 300 mg/L as CaCO₃), which require no further post-system treatment of water exiting the wetlands. Four TVA wetlands treat water with high Fe (>170 mg/L) and no net alkalinity. Two of these systems require NaOH treatment to comply with NPDES effluent limits, while two others use ALDs for further treatment of the effluent. A final TVA wetland system receives low Fe (<0.7 mg/L) and Mn (5.3 mg/L) and is ineffective in Mn removal. Based on their experience with these systems since 1985, Brodie (1993) suggests that staged aerobic wetland systems can accommodate Fe loads of up to 21 grams/m²/day even in the absence of excess alkalinity. Manganese loads up to 2 grams/m²/day can be accommodated, if alkalinity is present. Hedin et al. (1994) recommend for net alkaline water that wetlands be sized using 10 grams/m²/day for Fe and 0.5 grams/m²/day for Mn.

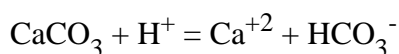
Analysis of 73 sites in Pennsylvania suggested that constructed wetlands are the best available technology for many postmining ground water seeps, particularly those of moderate pH (Hellier et al. 1994). However, those sites with net acidic discharges have a much lower successful treatment efficiency. For example, the Rougeux #1 site has a flow of 5.2 gpm and influent chemistry of 2.9 pH, 445 mg/L acidity as CaCO₃, Fe 45 mg/L, Mn 70 mg/L, and Al 24 mg/L. After flowing through a two-celled aerobic wetland, pH increased to 3.2, acidity was decreased by 43%, Fe by 50%, Mn by 17%, and Al by 83%. The wetland cost about \$15/m² to build in 1992 and was severely undersized. Although there is improvement in the water, the wetland effluent did not conform to effluent limits. Two other wetlands constructed on the site show similar results.

Anaerobic wetlands encourage water passage through organic rich substrates, which contribute significantly to treatment (Pictures 3 and 4). The wetland substrate may contain a layer of limestone in the bottom of the wetland or may mix the limestone among the organic matter. Wetland plants are transplanted into the organic substrate. These systems are used when the water has net acidity, so alkalinity must be generated in the wetland and introduced to the net acid water before dissolved metals will precipitate. The alkalinity can be generated in an anaerobic wetland system in two ways (Hedin and Nairn 1990). Certain bacteria, *Desulfovibrio* and *Desulfotomaculum*, can utilize the organic substrate (CH₂O, a generic symbol for organic carbon) as a carbon source and sulfate as an electron acceptor for growth. In the bacterial conversion of sulfate to hydrogen sulfide, bicarbonate alkalinity is produced:

 Image3.jpg (25370 bytes)

Alkalinity can also be generated as the limestone under the organic material reacts with acidity in the wetland:



The limestone continues to react when kept in an anaerobic environment because ferrous iron is relatively soluble at pH 7 in anoxic water and ferrous hydroxide does not form and coat the limestone. If ferrous iron is oxidized, forming ferric iron, then the ferric iron can hydrolyze and form ferric hydroxide, which then coats limestone when pH is above 3.0. Bacterial sulfate reduction and limestone dissolution produce water with higher pH and add bicarbonate alkalinity for metal removal.

Anaerobic wetlands promote metal oxidation and hydrolysis in aerobic surface layers, but also rely on subsurface chemical and microbial reduction reactions to precipitate metals and neutralize acid. The water infiltrates through a thick permeable organic subsurface sediment and becomes anaerobic due to high biological oxygen demand. Several treatment mechanisms are enhanced in anaerobic wetlands compared to aerobic wetlands, including formation and precipitation of metal sulfides, metal exchange and complexation reactions, microbially generated alkalinity due to reduction reactions, and continuous formation of carbonate alkalinity due to limestone dissolution under anoxic conditions. Since anaerobic wetlands produce alkalinity, their use can be extended to poor quality, net acidic, low pH, high Fe, and high dissolved oxygen (>2 mg/L) AMD. Microbial mechanisms of alkalinity production are likely to be of critical importance to long term AMD treatment. However, Wieder (1992) documents that the mechanism and efficiency of AMD treatment varies seasonally and with wetland age. Like their aerobic counterparts, anaerobic wetlands are most successful when used to treat small AMD flows of moderate water quality. At present, the sizing value for Fe removal in these wetlands is 10 grams/m²/day (Hedin and Nairn 1992).

Sorption onto organic materials (such as peats and soils) decreased Fe from 32 mg/L to 5 mg/L (84%), Mn from 15 to 14 mg/L (7%), and total suspended solids from 32 to 12 mg/L (63%), but eventually all sorption sites on substrate materials are exhausted by continual introduction of metals in acid water (Brodie et al. 1988). Kleinmann et al. (1991) suggested adsorption of metals by organic substrates may compensate for limited initial biological activity during the first few months of

operation in a new wetland system. A field study, which examined five wetland substrate types over a 25-month period, also demonstrated that organic substrates were saturated after only one to seven months of AMD input at 9 to 17 mg Fe per gram substrate (Wieder 1993). Although some natural inputs of organic matter occur annually at plant senescence, the adsorption capacity of a wetland is limited by saturation of all exchange sites. Substantial artificial inputs of organic matter have been used as a successful strategy to temporarily renew this adsorption capacity, following an observed decline in wetland performance (Eger and Melchert 1992, Haffner 1992, Stark et al. 1995).

Insoluble precipitates such as hydroxides, carbonates, and sulfides represent a major sink for metal retention in wetlands. About 50 to 70% of the total Fe removed from AMD by wetlands is found as ferric hydroxides (Henrot and Wieder 1990, Calabrese et al. 1991, Wieder 1992). Ferric hydroxide formation depends both on the availability of dissolved oxygen and on the initial oxidation state of Fe in the AMD. Wieder (1993) reported significant retention of ferric hydroxides in surface sediments of anaerobic wetlands.

Up to 30% of the Fe retained in wetlands may be found as ferrous iron and may be combined with sulfides (Calabrese et al. 1991, McIntyre and Edenborn 1990, Wieder 1992). Iron mono and disulfides form as a result of H_2S formation by microbial sulfate reduction in the presence of an oxidizable carbon source. In addition to its metal removal potential, sulfate reduction consumes acid and raises water pH (Hedin and Nairn 1992, Rabenhorst et al. 1992).

Long term retention of Fe sulfides and Fe hydroxides in a wetland is not well understood. Under continued anoxic conditions and in the absence of soluble Fe^{3+} , pyrite should remain stable. Calabrese et al. (1994) changed the influent of their anaerobic wetland from AMD to freshwater with no concomitant export of Fe^{2+} . The effluent pH was >6 due to continued limestone dissolution.

Some workers have indicated that wetland systems can be seeded with specially designed and selected microorganisms (Davison 1993, Phillips et al. 1994) to introduce or re-establish microbial activity. However, experiments utilizing appropriate controls have not established the efficacy of this approach (Calabrese et al. 1994). Experience with bioremediation of other wastes suggests that selection and enrichment of naturally occurring microbial populations is a superior, more cost-effective approach (Alexander 1993).

In constructed wetlands, higher plants serve several purposes including: substrate consolidation, metal accumulation, adsorption of metal precipitates, stimulation of microbial processes, wildlife habitat, and aesthetics. Wetland plant species vary in their ability to accumulate metals (Fernandes and Henriques 1990). Some reports document elevated tissue concentrations (Spratt and Wieder 1988), while others show little metal accumulation (Folsom et al. 1981). On an annual basis, uptake by *Typha* accounted for less than 1% of the Fe removed by volunteer wetlands treating AMD (Sencindiver and Bhumbla 1988).

Several studies report on the effects of different plant species in wetlands. Early in the development of treating AMD with constructed wetlands, *Sphagnum* was the predominant wetland species. *Sphagnum* has a well documented capacity to accumulate Fe (Gerber et al. 1985, Wenerick et al. 1989). However, Spratt and Wieder (1988) found that saturation of *Sphagnum* moss with Fe could occur within one growing season. Some have indicated that metal retention over the long term is limited in some wetlands because organic matter inputs by wetland plants are limited (Kleinmann 1990). Many of the original constructed wetlands were vegetated with *Sphagnum* but few remained

effective. Cattails (*Typha*) have been found to have a greater environmental tolerance than *Sphagnum* moss (Samuel et al. 1988). One of the reasons is that cattails do not accumulate metals into their tissues through uptake. Algae and a few other wetland species have also received attention due to the observation that enhanced metal removal was associated with algal blooms (Hedin 1989, Kepler 1988, Pesavento and Stark 1986, Phillips et al. 1994). In Colorado, algal mixtures were found to aerobically remove Mn from mine drainage (Duggan et al. 1992), presumably due to elevated pH resulting from algal growth and the extra oxygen generated photosynthetically by the algae. Probably the most important role that wetland plants serve in AMD treatment systems may be their ability to stimulate microbial processes. Kleinmann et al. (1991) explain that plants provide sites for microbial attachment, release oxygen from their roots, and supply organic matter for heterotrophs.

Long term successful treatment by a staged anaerobic wetland has also been reported for slightly net acidic water (Fe 89 mg/L; net acidity 40 mg/L as CaCO₃) at the Simco constructed wetland near Coshocton, OH (Stark et al. 1994). The wetland, built in 1985, has improved in treatment efficiency over time, not requiring any chemical treatment since 1990. The density of cattail shoots has increased to a current density of 17 shoots/m². Success at the Simco wetland is attributed to the presence of moderate mine water quality (near neutral pH and Fe <100 mg/L), sound wetland design, periodic site maintenance, and high vegetative cover.

Five anaerobic wetland systems in WV receiving 4 to 98 L/min of net acid water (110 to 2400 mg/L as CaCO₃ and Fe from 10 to 376 mg/L) reduced acidity by 3 to 76% and Fe concentrations by 62 to 80% (Faulkner and Skousen 1994). These wetlands were generally much smaller in area than that recommended by early formulas published by the U.S. Bureau of Mines (Hedin 1989) based on iron loads. For example, one of these wetlands, Keister, reduced the acidity of a 17-L/min flow from 252 to 59 mg/L as CaCO₃ (76% reduction) and increased pH from 3.1 to 5.4. Iron was reduced from 23 to 9 mg/L (62%), Mn from 23 to 20 mg/L (11%), and Al from 27 to 13 mg/L (52%). The Pierce wetland used an organic substrate over limestone and treated a 98-L/min flow. Influent pH was 3.3, acidity was 118 mg/L as CaCO₃, Fe of 10 mg/L, Mn of 8 mg/L, and Al of 9 mg/L. Outflow pH was 4.4, acidity was reduced to 57 mg/L as CaCO₃ (52%), Fe decreased to 2 mg/L (80%), Mn was reduced by 11%, and Al by 25%.

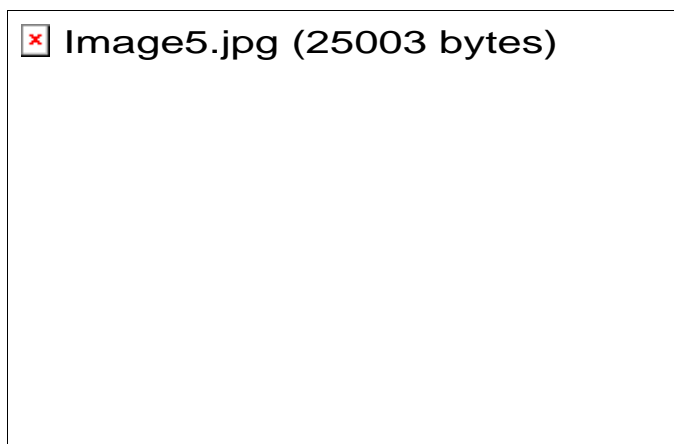
A wetland system consisting of six wetland cells (total area of 2500 m²) and a sedimentation basin each received a small flow (5 L/min) of AMD with pH of 3.0, acidity of 217 mg/L as CaCO₃, Fe of 27 mg/L, Al of 12 mg/L, and Mn of 2 mg/L (Hellier 1996). At this site in PA, the effluent after passing through the wetland was raised to pH 5.1, and the water contained a net acidity of 16 mg/L as CaCO₃, with about 46% iron removal, and 56% Al removal.

A 1022 m² surface flow wetland was constructed in KY to treat 37 L/min of AMD with a pH of 3.3, acidity of 2280 mg/L as CaCO₃, Fe of 962 mg/L, Mn of 11 mg/L, and Al of 14 mg/L (Karathanasis and Barton 1997). After construction in 1989, metal concentrations in the effluent were reduced during the first six months of treatment, however, the system failed thereafter due to insufficient wetland area and metal overloading. In 1995, a two-phase renovation project began incorporating the use of an ALD, and a series of anaerobic drains that promote vertical flow through limestone beds overlain by organic compost (much like a SAPS). Results to date indicate a pH of 6.4, slightly net alkaline water (15 mg/L as CaCO₃), Fe reduction of 96%, Mn removal of 50%, and Al by 100%.

A large anaerobic wetland located at Douglas, WV treated a 1000-L/min flow effectively for one year (Cliff et al. 1996). The influent pH was 3.0, with acidity of about 500 mg/L as CaCO_3 , Fe of 30 mg/L, and Al of 40 mg/L. An average net alkalinity of 127 mg/L as CaCO_3 was realized in the effluent water. Four years after installation, the original acidity of 500 mg/L as CaCO_3 is being reduced to between 250 to 300 mg/L as CaCO_3 . It has remained at this level of treatment for the past two years.

Anoxic Limestone Drains


Anoxic limestone drains (ALD) are buried cells or trenches of limestone into which anoxic water is introduced (Picture 5). The limestone dissolves in the acid water, 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 $\text{Fe}(\text{OH})_2$ at pH <6.0.




ALDs were first described by the Tennessee Division of Water Pollution Control (TDWPC) (Turner and McCoy 1990). TVA subsequently observed that AMD seeping through a coal refuse dam was being treated passively by limestone contained in an old haul road buried under the dam. Once the water containing excess alkalinity reached aerobic conditions at the ground surface, the metals oxidized and precipitated while the water remained near pH 6 (Brodie et al. 1990). TVA and TDWPC began building ALDs in 1989. Originally, ALDs were used for pre-treatment of water flowing into constructed wetlands. Brodie (1993) reported that ALDs improved the capability of wetlands to meet effluent limitations without chemical treatment. Since 1990, ALDs have also been constructed as stand-alone systems, particularly where AMD discharges from deep mine portals.

Longevity of treatment is a concern for ALDs, especially in terms of water flow through the limestone. If appreciable dissolved Fe^{3+} and Al^{3+} are present, clogging of limestone pores with precipitated Al and Fe hydroxides has been observed (Faulkner and Skousen 1994, Watzlaf et al. 1994). For waters with high sulfate (>1,500 mg/L), gypsum (CaSO_4) may also precipitate (Nairn et al. 1991). For an accepted design, no Fe^{3+} , dissolved oxygen (DO), or Al^{3+} should be present in the AMD. Selection of the appropriate water and environmental conditions is critical for long term alkalinity generation in an ALD. The maximum alkalinity that ALDs may generate is about 300 mg/L as CaCO_3 , although the specific level varies with water chemistry and contact time (Watzlaf and Hedin 1993).

Faulkner and Skousen (1994) reported both successes and failures among 11 ALDs treating mine water in WV. In all cases, water pH was raised after ALD treatment, but three of the sites had pH values <5.0 , indicating that the ALDs were not fully functioning or that the acid concentrations and flow velocities were too high for effective treatment. Water acidity in these drains, varying from 170 to 2200 mg/L as CaCO_3 , decreased 50 to 80%, but Fe and Al concentrations in the outflow also decreased. Ferric iron and Al^{3+} precipitated as hydroxides in the drains. With Fe and Al decreases in outflow water, some coating or clogging of limestone is occurring inside the ALD (Picture 6) and the water breaks out at the front of the ALD (Picture 7).

 Image6.jpg (19058 bytes)

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At the Brandy Camp site in PA, an ALD was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO_3 , Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1996). After passage through the ALD, the effluent had a pH of 6.0, net alkalinity of 10 mg/L as CaCO_3 , Fe of 50 mg/L, Mn of 10 mg/L, and Al of <1 mg/L. Most of the Fe and Mn passed through this system and precipitated in subsequent wetlands, while Al was precipitated inside the drain.


Since many sources of AMD have mixed amounts of Fe^{3+} and Fe^{2+} and some DO, utilization of an ALD under these conditions is not recommended. Current research involves pre-treating AMD by passing the water through a submerged organic substrate to strip oxygen from the water and to convert Fe^{3+} to Fe^{2+} . The pre-treated water is then introduced into an underlying bed of limestone


(see section 5.4; Kepler and McCleary 1994, Skousen, 1995). Like wetlands, ALDs may be a solution for treating specific types of AMD or for a finite period after which the system must be replenished or replaced.

Limestone has also been placed in 60-cm corrugated pipe and installed underground, and water is introduced into the pipe. Septic tanks have also been filled with limestone and AMD introduced into the tank. These applications have been used on steep slopes in lieu of buried cells or trenches, and on sites that have poor access and small water quality problems (Faulkner and Skousen 1995).

Successive Alkalinity Producing Systems

Successive alkalinity producing systems (SAPS) combine the use of an ALD and an organic substrate into one system (Kepler and McCleary 1994). Oxygen concentrations in AMD are often a design limitation for ALDs. In situations where DO concentrations are >1 mg/L, the oxygen must be removed from the water before introduction into an anoxic limestone bed. In a SAPS, acid water is ponded from 1 to 3 m over 0.2 to 0.3 m of an organic compost, which is underlain by 0.5 to 1 m of limestone (Picture 8). Below the limestone is a series of drainage pipes that convey the water into an aerobic pond where metals are precipitated. The hydraulic head drives ponded water through the anaerobic organic compost (Picture 9), where oxygen is consumed and ferric iron is reduced to ferrous iron. Sulfate reduction and Fe sulfide precipitation can also occur in the compost. Water with high metal loads can be passed through additional SAPS to reduce high acidity. Iron and Al clogging of limestone and pipes can be removed by flushing the system (Kepler and McCleary 1997). Data are still being gathered on the ability of SAPS to treat high Al water. Kepler and McCleary (1997) describe success with periodic flushing of Al precipitates from drainage pipes. One SAPS cited by them treat AMD containing 41 mg/L Al. However, Brodie (personal communication, 1997) described a SAPS receiving >40 mg/L Al at the Augusta Lake site in Indiana being plugged with Al precipitates after 20 months despite flushing. Successful SAPS have used mushroom compost, while other types of organic material have problems with plugging. Many possible variations in composition and thickness of organic matter, including the addition of limestone, desirability of promoting sulfate reduction, flow rates through organic matter, time schedule for replacement or addition of new organic matter, and precipitation of siderite in the limestone remain to be investigated.

 Image8.jpg (30003 bytes)

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Kepler and McCleary (1994) reported on initial successes for three SAPS in PA. The Howe Bridge SAPS reduced acidity from 320 mg/L to 93 mg/L as CaCO_3 , and removed 2 mg/L ferric iron. The REM SAPS decreased acidity from 173 to 88 mg/L as CaCO_3 , and exported more ferrous iron than entered. The Schnepf Road SAPS decreased acidity from 84 to 5 mg/L as CaCO_3 , but removed all 19 mg/L ferric iron, with only 1 mg/L ferrous iron exiting the wetland.

Kepler and McCleary (1997) reported the use of SAPs in OH, PA, and WV. In all cases, Al in AMD precipitated in their systems. Their drainage design incorporates a flushing system called the 'Aluminator' (Picture 10). This allows for the precipitated Al to be flushed from the pipes thereby maintaining hydraulic conductivity through the limestone and pipes. One SAPS, Buckeye, received 3 L/min of very acid water (pH of 4.0, acidity of 1989 mg/L as CaCO_3), Fe of 1005 mg/L, and Al of 41 mg/L. Over a two-year period, the effluent had a pH of 5.9, net acidity concentration of about 1000 mg/L, Fe of 866 mg/L, and <1 mg/L Al. A second site, Greendale, treated a 25-L/min flow, and increased the pH from 2.8 to 6.5, changed the water from a net acid water (925 mg/L as CaCO_3) to a net alkaline water (150 mg/L as CaCO_3), Fe from 40 to 35 mg/L, and Al from 140 to <1 mg/L.

 Image10.jpg (32842 bytes)

At the Brandy Camp site in PA, a SAPS was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO_3 , Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier 1996). After passage through the SAPS, the effluent had a pH of 7.1, net alkalinity of 115 mg/L as CaCO_3 , Fe of 3 mg/L, Mn of 10 mg/L, and Al of <1 mg/L. The system effectively increased alkalinity, but retained most of

the Fe and Al inside the system. Longevity of treatment is a major concern for ALDs, especially in terms of water flow through the limestone. Eventual clogging of the limestone pore spaces with precipitated Al and Fe hydroxides, and gypsum (CaSO_4) is predicted (Nairn et al. 1991). For optimum performance, no Fe^{+3} , dissolved oxygen (DO), or Al should be present in the AMD. Selection of the appropriate water and environmental conditions is critical for long-term alkalinity generation in an ALD.

Limestone Ponds

Limestone ponds are a new passive treatment idea in which a pond is constructed on the upwelling of an AMD seep or underground water discharge point (Picture 11). Limestone is placed in the bottom of the pond and the water flows upward through the limestone (Faulkner and Skousen 1995). Based on the topography of the area and the geometry of the discharge zone, the water can be from 1 to 3 m deep, containing 0.3 to 1 m of limestone immediately overlying the seep. The pond is sized and designed to retain the water for 1 or 2 days for limestone dissolution, and to keep the seep and limestone under water. Like ALDs, this system is recommended for low DO water containing no Fe^{3+} and Al^{3+} . However, the advantage of this system is that the operator can observe if limestone coating is occurring because the system is not buried. If coating occurs, the limestone in the pond can be periodically disturbed with a backhoe to either uncover the limestone from precipitates or to knock or scrape off the precipitates. If the limestone is exhausted by dissolution and acid neutralization, then more limestone can be added to the pond over the seep. Three limestone ponds have been installed but no information is available on their treatment.


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Open Limestone Channels

Open limestone channels (OLCs) introduce alkalinity to acid water in open channels or ditches lined with limestone (Ziemkiewicz et al. 1994). Acid water is introduced to the channel and the AMD is treated by limestone dissolution (Picture 12). Past assumptions have held that armored limestone (limestone covered or coated with Fe or Al hydroxides) ceased to dissolve, but experiments show that coated limestone continues to dissolve at 20% the rates of unarmored limestone (Pearson and McDonnell 1975). Recent work has demonstrated that the rate for armored limestone may be even higher (Ziemkiewicz et al. 1997). The length of the channel and the channel gradient, which affects turbulence and the buildup of coatings, are design factors that can be varied for optimum performance (Picture 13). Optimum performance is attained on slopes exceeding 20%, where flow velocities keep precipitates in suspension, and clean precipitates from limestone surfaces. In appropriate situations,

OLCs are being implemented for long term treatment. Utilizing OLCs with other passive systems can maximize treatment and metal removal (Picture 14).

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 **Image14.jpg (21530 bytes)**

 **Image13.jpg (29393 bytes)**

Among the questions still to be investigated are the behavior of OLCs in waters of different pH and high heavy metal loads (like metal mine drainage), possible interactions of slope with water chemistry, and the possible importance of limestone purity.

Ziemkiewicz et al. (1997) found armored limestone in a series of laboratory experiments was 50 to 90% as effective as unarmored limestone in neutralizing acid. Seven OLCs in the field reduced acidity in AMD by 4 to 205 mg/L as CaCO_3 , at rates of 0.03 to 19 mg/L per meter of channel length. The highest removal rates were with channels on slopes of 45 to 60% and for AMD with acidity of 500 to 2600 mg/L as CaCO_3 . For example, the Eichleberger OLC was 49 m long on a slope of 20%, and received about 378 L/min of 510 mg/L acidity as CaCO_3 . After flowing down the channel, the acidity was decreased to 325 mg/L as CaCO_3 (36% decrease). The PA Game Commission OLC was only 11 m in length on a 45% slope, and received 484 L/min of 330 mg/L acidity as CaCO_3 . The water acidity at the end of the channel was 125 mg/L as CaCO_3 (62% decrease).

Three OLCs were installed in the Casselman River Restoration project (Ziemkiewicz and Brant 1996). One OLC, 400 m long on a 8% slope, received 60 L/min of pH 2.7 water, 1290 mg/L as CaCO_3 acidity, 622 mg/L Fe, 49 mg/L Mn, and 158 mg/L Al. The effluent pH over a two year period was 2.9, acidity was 884 mg/L as CaCO_3 (31% decrease), Fe was 210 mg/L (66% removal), Mn was 42 mg/L (14% decrease), and Al was 103 mg/L (35% decrease).

At the Brandy Camp site in PA, a 15-m-long OLC on a 10% slope was employed to treat AMD with a pH of 4.3, acidity of 162 mg/L as CaCO_3 , Fe of 60 mg/L, Mn of 10 mg/L, and Al of 5 mg/L (Hellier, case study 1997). After passage through the OLC, the effluent had a pH of 4.8, net acidity of 50 mg/L as CaCO_3 , Fe of 17 mg/L, Mn of 8 mg/L, and Al of 3 mg/L. The OLC removed 72% of the Fe and about 20% of the Mn and Al from the water.

Bioremediation

Bioremediation of soil and water involves the use of microorganisms to convert contaminants to less harmful species in order to remediate contaminated sites (Alexander 1993). Microorganisms can aid or accelerate metal oxidation reactions and cause metal hydroxide precipitation. Other organisms can promote metal reduction and aid in the formation and precipitation of metal sulfides. Reduction processes can raise pH, generate alkalinity, and remove metals from AMD solutions. In most cases, bioremediation of AMD has occurred in designed systems like anaerobic wetlands where oxidation and reduction reactions are augmented by special organic substrates and limestone. In a few cases, substrates have been incorporated into spoils to aid in in-situ treatment of water by the use of indigenous microorganisms.

A mixture of organic materials (sawdust and sewage sludge) was emplaced into a mine spoil backfill to stimulate microbial growth and generate an anoxic environment through sulfate reduction. The results of the organic matter injection process caused no change in water pH, about a 20% decrease in acidity (1500 to 1160 mg/L as CaCO_3 , and a similar decrease in Fe, Mn, and Al. The results indicate that the process works, but improvements in organic material injection and the establishment of a reliable saturated zone in the backfill are needed for maximum development (Rose et al. 1996).

The Lambda Bio-Carb process is a bioremediation system utilizing site-indigenous, mixed microorganism cultures selected for maximum effectiveness (Davison 1993). On a field site in PA using this bioremediation process, Fe in AMD was decreased from 18 mg/L to < 1 mg/L, Mn declined from 7 mg/L to 2 mg/L, and pH increased from around 6.0 to 8.0.

The Pyrolusite process uses selected groups of microorganisms growing on limestone to oxidize Fe and Mn into their insoluble metal oxides (Vail and Riley 1997). On a field site in PA using a limestone bed inoculated with microorganisms, Fe was decreased from 25 mg/L to < 1 mg/L, Mn went from about 25 mg/L to < 1 mg/L, while pH and alkalinity in the effluent were increased.

Diversion Wells

The diversion well is a simple device initially developed for treatment of stream acidity caused by acid rain in Norway and Sweden (Arnold 1991). It has been adopted for AMD treatment in the eastern USA. A typical diversion well consists of a cylinder or vertical tank of metal or concrete, 1.5-

1.8 m in diameter and 2-2.5 m in depth, filled with sand-sized limestone (Picture 15). This well may be erected in or beside a stream or may be sunk into the ground by a stream. A large pipe, 20-30 cm in diameter, enters vertically down the center of the well and ends shortly above the bottom (Picture 16). Water is fed to the pipe from an upstream dam or deep mine portal with a hydraulic head of at least 2.5 m (height of well). The water flows down the pipe, exits the pipe near the bottom of the well, then flows up through the limestone in the well, thereby fluidizing the bed of limestone in the well. The flow rate must be rapid enough to agitate the bed of limestone particles. The acid water dissolves the limestone for alkalinity generation, and metal flocs produced by hydrolysis and neutralization reactions are flushed through the system by water flow out the top of the well. The churning action of the fluidized limestone also aids in limestone dissolution and helps remove Fe oxide coatings so that fresh limestone surfaces are always exposed. Metal flocs suspended in the water are precipitated in a downstream pond.

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 Image16.jpg (17918 bytes)

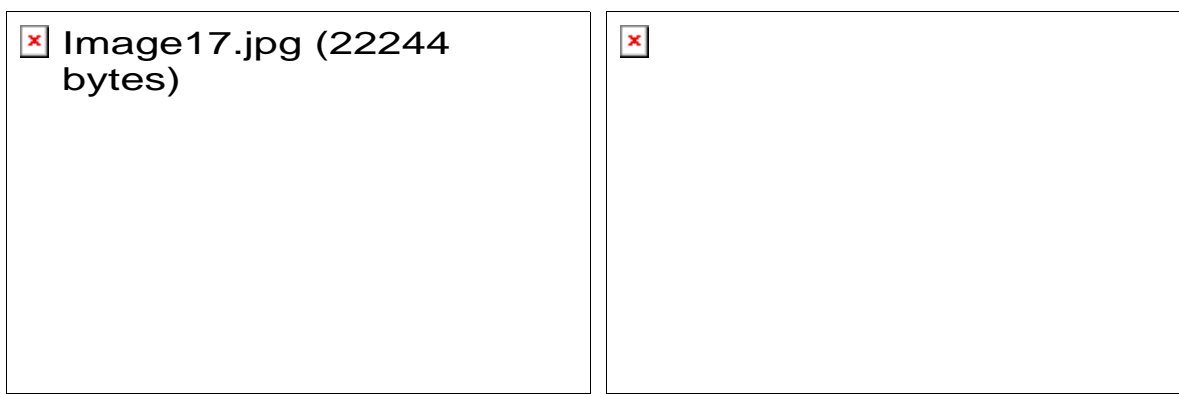
Arnold (1991) used diversion wells for AMD treatment in PA and reports that three wells increased pH from 4.5 to 6.5, with corresponding decreases in acidity. For example, one diversion well located at Lick Creek treats about 1000 L/min of slightly acid water. After passing through the diversion well, the pH changes from 4.5 to 5.9 and the net acid water (8 mg/L as CaCO_3) changes to net alkaline water (6 mg/L as CaCO_3). Similar results are found for several other sites in PA.

Diversion wells have also been constructed in the Casselman River Restoration Project (Ziemkiewicz and Brant 1996). This large diversion well has a retention time of about 15 min for a 360-L/min flow of moderately acid water. The diversion well reduces the acidity from 314 to 264 mg/L as CaCO_3 , Fe from 83 to 80 mg/L, and Al from 24 to 20 mg/L.

At the Galt site in WV, a diversion well changes a 20-L/min flow from a pH of 3.1 to 5.5, acidity from 278 to 86 mg/L as CaCO₃, Fe from 15 to 2 mg/L, and Al from 25 to 11 mg/L (Faulkner and Skousen 1995).

Limestone Sand Treatment

Sand-sized limestone may also be directly dumped into AMD streams at various locations in watersheds (Picture 17). The sand is picked up by the streamflow and redistributed downstream, furnishing neutralization of acid as the stream moves the limestone through the streambed. The limestone in the streambed reacts with the acid in the stream, causing neutralization. Coating of limestone particles with Fe oxides can occur, but the agitation and scouring of limestone by the streamflow keep fresh surfaces available for reaction.



The WV Division of Environmental Protection treats 41 sites in the Middle Fork River, including the headwaters of 27 tributaries (Zurbuch 1996). The first year's full treatment was based on four times the annual acid load for non-AMD impacted streams and two times the load for AMD tributaries. During subsequent years, limestone sand application will be an amount equal to the annual acid load, or about 2,000 tons/yr. About 8,000 tons of limestone were deposited among the 41 sites in 1995. Water pH has been maintained above 6.0 for several miles downstream of the treatment sites. The anticipated precipitate coating of the limestone was not observed. It is predicted that treating the river with limestone sand will be necessary three times a year to maintain water quality for fish populations.

Acknowledgments

This paper is the second section in "Acid Mine Drainage Control and Treatment," a chapter in a new book entitled "Reclamation of Drastically Disturbed Lands," being prepared by the American Society for Agronomy and the American Society for Surface Mining and Reclamation. The anticipated release date for this book is 1998. The author thanks Tiff Hilton, Ben Faulkner, Alan Sexstone, Paul Ziemkiewicz, Robert Darmody, John Sencindiver, Tim Phipps, Jerry Fletcher, Keith Garbutt, Bill Hellier, Art Rose and two anonymous reviewers for helpful comments during the review process. Acid mine drainage research at West Virginia University is supported by grants from the College of Agriculture and Forestry, the National Mine Land Reclamation Center, the USDI Bureau of Mines, the West Virginia Division of Environmental Protection, and from funds appropriated by the Hatch Act.

[References](#)

**MEND Report 3.14.1
1996, Revised 1999
Review of Passive Systems for Treatment
of Acid Mine Drainage**

Please see MEND Report included as separate file on disk

C. Zipper and C. Jagie
2001
Passive Treatment of Acid-Mine Drainage
with Vertical-Flow Systems



Passive Treatment of Acid-Mine Drainage with Vertical-Flow Systems



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Introduction

The purpose of this publication is to present guidance for the design and construction of vertical-flow systems for the passive treatment of acid mine drainage (AMD). The term "passive treatment" refers to methods of treating AMD that rely on biological, geochemical, and gravitational processes. Passive systems do not require the constant input of chemical reagents that are characteristic of "active" AMD

treatment.

This publication is intended to help potential users determine whether or not a vertical-flow passive treatment system should be considered for a specific AMD discharge. Should the reader decide to proceed, the reader is encouraged to engage the services of a professional with passive-system design and construction experience, especially if the system is intended to meet specific effluent criteria.

These guidelines reflect results of recent research and current practices. AMD treatment technology is developing rapidly as more is learned about how these systems function. Prior to engaging in a vertical-flow AMD-treatment project, readers are advised to access the on-line version of this publication, available through both Virginia Cooperative Extension <http://www.ext.vt.edu/resources/> and the Powell River Project <http://als.cses.vt.edu/prp/>, for reference to updated design guidance as it becomes available.

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Overview of Vertical Flow Systems

Vertical-flow systems have also been given a variety of names over the years such as: SAPS (for "successive alkalinity producing systems," Kepler and McCleary, 1994), RAPS (for "reducing and alkalinity producing systems," Watzlaf and others, 2000), and APS (for "alkalinity producing systems," Skousen and Ziemkiewicz, 1995). In 1987, A.C. Hendricks developed a vertical-flow system at Galax, Virginia, to treat the effluent from a long-abandoned pyrite mine (Hendricks, 1991). In 1990, Westmoreland Coal Company and A.C. Hendricks developed a vertical-flow system in Wise County, Virginia, working through Powell River Project (Duddleston and others, 1992). Kepler and McCleary (1994) developed similar systems in Pennsylvania. They are also largely responsible for the widespread use of vertical-flow systems in northern Appalachia, and the development of several design advances.

When properly designed, constructed, and maintained in appropriate situations, vertical-flow treatment offers advantages relative to other means of treating AMD. Unlike active treatment, vertical-flow systems do not require the purchase of chemical reagents or storage of chemical reagents on site. Although vertical-flow systems do require more area and volume than active systems sized with equivalent treatment capacity, they require far less area than other "wetland" systems. Vertical-flow systems are generally ineffective in removing Mn, but passive treatment methods for removing Mn from mine-discharge waters are currently being developed (Kerrick and Horner, 1998; Brent and Ziemkiewicz, 1997; Sikora and others, 1996). These systems can, however, be very effective in pre-treating AMD prior to an active treatment finishing process, which may reduce the total costs of meeting regulatory standards.

Even where Mn is not a problem, vertical-flow treatment systems should not be considered as either a stand-alone or a walk-away AMD-treatment solution. This publication describes how vertical-flow treatment can be integrated with other passive-treatment elements to provide AMD treatment, and it presents guidelines for vertical-flow system design.

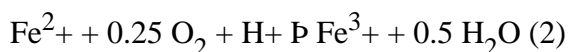
Although vertical-flow systems do require periodic attention and maintenance, they can be maintained on a week-to-week basis with less time and expense than conventional active systems. Operators should expect, however, that a vertical flow system in a long-term application will require renewal via replacement of major system elements. Current design practice assumes 20- to 25-year

lifespans for these systems. As of this writing, at least two vertical-flow systems have operated successfully over periods approaching 10 years (Pine Branch in Virginia, and Howe Bridge in western Pennsylvania) without requiring renewal of major system elements. Many other systems have operated successfully over shorter periods, while still others have failed to meet treatment goals due to inadequate design.

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Acid Mine Drainage

Acidic mine drainage (AMD) is an environmental pollutant of major concern in mining regions throughout the world. AMD occurs as a result of the oxidation of sulfide minerals when they are exposed to oxygen and water during the mining process. In coal-mining areas, the most common of these minerals is pyrite (FeS_2). The process for AMD formation is commonly represented by the following reactions:



The process is initiated with the oxidation of pyrite and the release of ferrous iron (Fe^{2+}), sulfate, and acidity (Eq. 1). The sulfide-oxidation process is accelerated by the presence of Thiobacillus bacteria. Ferrous iron then undergoes oxidation forming ferric iron (Fe^{3+}) (Eq. 2). Finally, Fe^{3+} reacts with H_2O (is hydrolyzed), forming insoluble ferric hydroxide (FeOOH), an orange-colored precipitate, and releasing additional acidity (Eq. 3). The FeOOH formation process is pH-dependent, and occurs rapidly when pH is greater than 4.

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Passive Treatment of AMD

[Figure 1](#)

Passive treatment systems are typically modeled after wetlands and other natural processes, with modifications directed toward meeting specific treatment goals. Early research included investigations of natural Sphagnum sp. peat wetlands that were receiving AMD (Weider, 1982). These systems were able to raise pH and lower iron concentrations without visible deterioration.

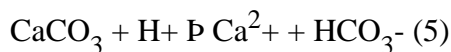
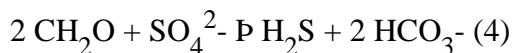
Aerobic Wetlands

One of the first designs put into use was a shallow (± 1 foot), surface flow wetland planted with cattails (*Typha* sp.) (Hedin and others, 1994a; Skousen and others, 1998; Skousen and others, 2000). Substrates for these wetlands varied from natural soils to composted organic matter. These "aerobic" wetlands aerated the mine waters flowing among the vegetation. This allowed for the oxidation of

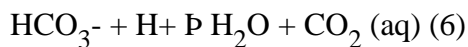
Fe^{2+} and its subsequent deposition as FeOOH . Aerobic wetlands are typically used to treat mildly acidic or net-alkaline waters containing elevated Fe concentrations. Published design criteria for Fe removal are up to 310 mg/day per square-foot on sites where the discharge is intended for regulatory compliance, and up to 620 mg/day per square-foot where regulatory compliance is not an issue (Hedin and others, 1994a). Where waters are net-alkaline and Fe is not a problem, aerobic wetlands have also proved capable of removing Mn, but very large areas are needed. Use of aerobic wetlands for Fe removal generally causes pH to decline due to the generation of proton acidity by Fe hydrolysis (Eq. 3) (Skousen and others, 1997).

Anaerobic Wetlands

Modifications of the aerobic wetland design were made to raise water pH and increase metal precipitation. These included the addition of a bed of limestone beneath an organic substrate (Hedin and others, 1994a). This design encouraged the generation of bicarbonate alkalinity (HCO_3^-) by both anaerobic microbial sulfate reduction (Eq. 4, with CH_2O representing biodegradable organic compounds) and limestone dissolution (Eq. 5).



The bicarbonate neutralizes the acidity of the AMD, thereby raising pH (Eq. 6) and increasing the precipitation of acid-soluble metals such as Fe.



Anaerobic wetlands have proved capable of removing Fe and producing alkalinity. Hedin and others (1994a) reported average Fe removal rates of up to 1300 mg/day per square-foot, but these systems are limited in capability to raise pH, especially where Fe is present. The primary factor limiting their effectiveness is the slow mixing of the alkaline substrate water with acidic waters near the surface. This slow mixing can be overcome by constructing very large wetlands to provide long retention times (Skousen and others, 1997). This demand on land area is a major impediment to the increased use of these systems by mine operators with limited space for wetland construction.

Current guidelines for the construction of anaerobic wetlands advocate use of a 1- to 2- foot layer of organic matter over a 0.5- to 1- foot bed of limestone with a surface water depth of 1 to 3 inches. At water levels deeper than 2 to 3 inches, growth of wetland vegetation is hindered. The organic matter must be permeable to water and biodegradable; spent mushroom compost has been used successfully at a number of sites in northern Appalachia. For greater effectiveness, limestone may be mixed in with the organic matter. Cattails (*Typha* sp.) may be planted throughout the wetland to supply additional organic matter for heterotrophic bacteria and to promote metal oxidation with the release of oxygen from their root system (Skousen and others, 1997). Available guidelines for system sizing recommend planning for acidity removal rates 100 mg/day per square-foot for systems designed to achieve regulatory compliance, and up to 200 mg/day per square-foot where regulatory compliance is not a concern. For a more thorough review of anaerobic wetlands, see either Hedin and others (1994a) or Skousen and others (2000).

Anoxic Limestone Drains

One method used to reduce wetland size is pre-treatment of the AMD using anoxic limestone drains (ALDs). ALDs are limestone-filled trenches that can rapidly produce bicarbonate alkalinity via limestone dissolution. They are installed at the point of discharge to capture the AMD subterraneously. ALDs are capped with clay or compacted soil to prevent AMD contact with oxygen (Hedin and Watzlaf, 1994). The acidic water flowing through trench dissolves the limestone and releases bicarbonate alkalinity (Eq. 5). These systems have demonstrated capabilities to raise the alkalinity and/or neutralize acidity by as much as 300 mg/L (CaCO₃ equivalent) with retention times of only 14 - 23 hours (Hedin and Watzlaf, 1994, Hedin and others, 1994a), although net-alkalinity generation rates of 150 to 250 mg/L are more typical. The effluent is discharged into a settling pond to allow for acid neutralization, pH adjustment, and metal precipitation. ALD pretreatment of AMD allows for the construction of smaller, more effective treatment systems due to the decreased metal loadings and increased alkalinity of the ALD effluent discharged into them.

ALDs, however, are not capable of treating all discharges. Significant concentrations of Al or Fe⁺³ in the discharge can cause an ALD to clog with metal-hydroxides once a pH of 4.5 or above is reached (Hedin and others, 1994a). When excess Fe⁺³ is present in the AMD, or is allowed to form from Fe⁺² due to the presence of O₂, formation of solid FeOOH can occur within the ALD (Eq. 3). Ideally, Fe⁺³, Al, and dissolved O₂ concentrations of waters being treated by an ALD would all be below 1 mg/L. However, AMD is not always ideal. Skousen and others (2000) state that ALDs have been used successfully for AMD with dissolved oxygen concentrations of up to 2 mg/L and Al concentrations of up to 25 mg/L, when less than 10 percent of total Fe in the Fe⁺³ form. If Al is present at a concentration greater than 1 mg/L and waters in the ALD reach a pH of 4.5 or above, Al will precipitate as Al(OH)₃. Both FeOOH (eq. 3) and Al(OH)₃ precipitation generate acidity.



ALD systems will also fail if Fe³⁺ precipitates on the limestone surface, thus limiting its dissolution, a process known as "armoring." In low dissolved oxygen ("anoxic") environments, the Fe²⁺ form of iron predominates and does not form a coating on the limestone or interfere with limestone dissolution (Hedin and others, 1994a; Watzlaf, 1997). A thorough reference for the design and sizing for ALDs can be found in Hedin and Watzlaf (1994).

Vertical Flow Systems

Vertical flow systems combine the treatment mechanisms of anaerobic wetlands and ALDs in an attempt to compensate for the limitations of both (Kepler and McCleary, 1994). The basic elements of these systems are similar to the anaerobic wetland, but a drainage system is added within the limestone layer to force the AMD into direct contact with both the organic matter and the limestone.

The three major vertical-flow system elements are the drainage system, a limestone layer, and an organic layer. The system is constructed within a water-tight basin, and the drainage system is constructed with a standpipe to regulate water depths and ensure that the organic and limestone layers remain submerged. As the AMD waters flow downward through the organic layer, two essential functions are performed: dissolved oxygen in the AMD is removed by aerobic bacteria utilizing biodegradable organic compounds as energy sources, and sulfate-reducing bacteria in the anaerobic

zone of the organic layer generate alkalinity (Eq. 4). Low DO concentrations, biodegradable carbon, and the presence of dissolved sulfate are necessary for sulfate-reduction to take place. An organic layer capable of removing DO to concentrations below 1 mg/L is essential to prevent limestone armoring. In the limestone layer, CaCO_3 is dissolved by the acidic, anoxic waters moving down to the drainage system, producing additional alkalinity. The final effluent is discharged from the drainage system standpipe into a settling pond to allow acid neutralization and metal precipitation prior to ultimate discharge.

In order to avoid clogging of the limestone layer with Fe^{+3} and Al precipitants (Eqs. 3 and 7), a valved flushing pipe is typically included as a part of the drainage system (Kepler and McCleary, 1997). When opened, this valved drain discharges at a lower elevation than the standpipe. Head pressure (usually, 6 to 10 feet) caused by the standing water in the system moves waters through the system rapidly, flushing the gel-like forms of Al and Fe ("floc") that accumulates in the drainage pipes and limestone pores. Opening this valve periodically removes the loose metal hydroxide floc and discharges it into the settling pond.

Current practices include a limestone layer of 2 to 3 feet in depth, an organic layer of 6 to 12 inches in depth, and a standpipe and basin capable of maintaining a 3- to 5-foot deep body of water above the organic layer (Skovran and Clouser, 1998; Kepler and McCleary, 1994). Building systems with 3 feet or more of standing water over the mulch layer provides sufficient head-pressure and aids flushing.

For severe AMD discharges, several vertical-flow systems can be linked in series to generate alkalinity successively until the treatment goals are reached.

Open Limestone Channels

Where AMD must be conveyed over some distance prior to or during treatment, use of open channels lined with limestone has been shown to be an effective mechanism for removing Fe and generating small amounts of alkalinity (Ziemkiewicz and others, 1997). Even though the limestone in such channels typically becomes armored with Fe, research indicates that the armored limestone retains some treatment effectiveness. Open limestone channels are most effective when placed on slopes of greater than 20%, as the abrasive action of fast-moving water tends to dislodge the armoring Fe. Open limestone channels can be effective as one element of a passive treatment system, but typically are not relied upon for stand-alone AMD treatment.

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Developing a Passive Treatment Strategy

AMD Characterization

The design of all passive treatment systems starts with characterization of influent AMD chemistry and flow. Prior to designing a passive treatment system, a complete characterization of influent AMD is needed to determine which type of system is appropriate and how to design that system to meet treatment goals.

Regular sampling over at least a 12-month period is recommended to account for the variations that may occur or in response to seasonal changes or storms. At a minimum, all water samples should be analyzed for pH, total Fe, Mn, Al, SO_4^{2-} , total alkalinity and total acidity. Additional analyses,

including Fe^{+2} , Fe^{+3} , and dissolved oxygen, are necessary if an anoxic limestone drain is being considered as a treatment option. Dissolved oxygen and pH should be measured on-site. Dissolved oxygen measurements are sensitive, and experience by the sampling personnel is necessary to obtain an accurate reading. Samples designated for metals analysis should be filtered at the time of sampling to remove particulate matter and acidified to $\text{pH} < 2$ (APHA, 1985). Acidity and alkalinity samples should be placed on ice immediately following sampling and analyzed within 24 hours. Flow measurements should also be taken on all sampling dates.

Based on water-sampling data, a "design" water quality condition should be established. This will generally be the worst-case condition, as defined relative to regulatory standards, if the AMD discharge is intended to achieve regulatory compliance. The water sampling procedures should assure that a variety of weather and climate conditions are represented, to ensure that the resultant data provide a realistic assessment of the design conditions. Average and maximum influent flow should also be estimated for use in the design process.

Passive Treatment System Selection

The selection of a passive treatment system is governed by influent water quality and site characteristics. The diagram in [Figure 2](#) illustrates a decision process for selecting an appropriate system for a given discharge (Hedin and others, 1994a; Skousen and others, 1998). For net alkaline discharges containing elevated concentrations of Fe, no additional alkalinity additions are needed. The only conditions necessary to complete treatment are an oxidizing environment and sufficient residence time to allow for metal oxidation and precipitation. These conditions can be provided by a settling pond; if sufficient area is available, the settling pond may be followed by an aerobic wetland.

The treatment of net acidic drainage can be handled in a number of ways depending on influent chemistry. If the influent quality is suitable for an ALD, an ALD can be employed as a pretreatment method. A post-ALD settling pond or aerobic wetland is required to allow for the oxidation and precipitation of metals.

Acidic waters that are not suitable for ALDs can be treated with either an anaerobic wetland or a vertical flow system. Due to the potentially large demands on land area of anaerobic wetlands, they are usually only practical for low-flow situations. For systems that receive water that has a pH greater than 4, settling ponds may precede an anaerobic wetland cell to remove significant quantities of Fe. The remaining discharges can be treated using a vertical-flow system.

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Vertical-Flow System Design

Vertical-flow passive treatment systems are able to neutralize acidity and promote metal precipitation in difficult treatment situations. Due to the active mixing of the AMD with the limestone, acid neutralization is more rapid in vertical-flow systems than in anaerobic wetlands, and thus vertical-flow systems require shorter residence times and smaller surface areas. These systems are not stand-alone, but require the addition of an oxidation/settling pond at the effluent point to allow for the precipitation and storage of the metals in solution. For discharges containing significant quantities of Fe^{+3} , vertical-flow systems should be preceded by either a settling pond or an aerobic wetland if sufficient land area is available. The removal of such metals prior to vertical-flow treatment will lengthen the system's useful life and reduce necessary maintenance by limiting accumulation of

metal-hydroxide precipitants on the organic matter surface. A settling pond should also precede the system if incoming waters contain sediment.

Guidelines reported by Skovran and Clouser (1998), Skousen and others (1998) and Kepler and McCleary (1994) provide a general form for design of these systems.

Sizing the Limestone Layer

Although per-unit-area Fe removal-rates are typically applied in designing "wetland" treatment systems, per-unit-area rates of alkalinity generation by installed vertical-flow systems vary. Research has demonstrated the presence of relationships between influent water quality, AMD residence time in the limestone layer, and alkalinity generation (Jage and others, 2000). The primary factor governing alkalinity generation by most vertical-flow systems is the rate at which limestone dissolves relative to the rate at which AMD moves through the system. Residence-time of the AMD in the limestone layer is one factor governing alkalinity generation. Limestone dissolves most rapidly during the first few hours of AMD contact. As the waters in contact with the limestone become saturated with dissolved Ca^{2+} and HCO_3^- , the rate of limestone dissolution slows considerably. Another factor governing the rate at which limestone dissolves is pH; at lower pH, CaCO_3 dissolves more rapidly.

Research has developed a model that can be used to estimate vertical flow systems' alkalinity generation rates as a function of AMD residence time within the limestone layer and AMD concentrations of Fe and non-Mn acidity (Jage and others, 2001; see Eq. 9 below). Given the volume and quality of the AMD to be treated, this model can be used to estimate the size of the limestone layer required to generate a given quantity of alkalinity. We recommend that the model be used to provide a design minimum, but that systems be constructed larger than indicated by the model whenever possible. Increasing the size of a vertical-flow system will increase the probability of successful treatment.

Calculating a Preliminary Limestone Volume

The first step in the system sizing process is to determine the size of the limestone layer and number of vertical-flow cells needed for adequate treatment. We recommend that the system be sized to generate alkalinity sufficient to offset incoming non-Mn acidity, plus additional alkalinity so as to achieve a factor of safety. We recommend sizing the system to generate at least 100 mg/L of alkalinity, over and above the amount needed to offset influent non-Mn acidity when sufficient land area is available, so as to provide a reasonable probability of successful treatment. Non-Mn acidity can be calculated as:

$$\text{Non-Mn Acidity} = \text{Acidity} - 1.818 * \text{Mn} \quad (8)$$

where,

Acidity = Total Acidity (mg/L as CaCO_3) of the design influent water quality

Mn = Manganese concentration (mg/L) of the design influent water quality

Non-Mn Acidity = acidity derived from Al, Fe, H^+ and other ions (mg/L as CaCO_3)

Once the design rate of alkalinity generation has been determined, the limestone residence time of a system can be estimated using the equation below:

$$\text{Alknet} = 99.3 * \log_{10}(t_r) + 0.76 * \text{Fe} + 0.23 * \text{Non-Mn Acidity} - 58.02 \quad (9)$$

where,

Alknet = net alkalinity to be generated (mg/L as CaCO₃)

Fe = total iron concentration (mg/L) of the design influent water quality

Non-Mn Acidity = non-manganese acidity (mg/L as CaCO₃ - see equation 8)

t_r = average residence time in the limestone layer (hours).

Equation 9 ("the model") can be solved mathematically for t_r, if the reader is so inclined, or the reader may choose to estimate a residence time that may be achievable based on site conditions and use the model to determine whether or not a system built with such a residence time is likely to be adequate for treatment of the design AMD discharge. [Figure 3](#) represents Equation 9's predictions for a sample influent water quality.

This model is intended for application to systems built with high-calcium limestone in the 4-to-6 inch size range. High-calcium limestone contains more than 90% CaCO₃ and is more soluble than limestone that contains appreciable quantities of Mn. The CaCO₃ residence time that results from solving Equation 9 should be adjusted to account for limestone dissolution as the system ages (see below). The model was developed by analyzing data from vertical flow systems receiving influent waters with Fe concentrations less than 300 mg/L and non-Mn acidity concentrations of less than 500 mg/L (Jage and others, 2001). The model has not been tested for drainages where Al concentrations exceed 60 mg/L.

Equation 9 is not expected or intended to give precise results. [Figure 4](#) shows the relationship of predicted alkalinity generation to observed generation for 18 vertical flow cells. All values plotted are system averages over periods exceeding one year. The plots for Howe Bridge and the Oven Run systems were calculated from system averages published by Watzlaf and others (2000), while all other system averages were calculated from monthly observations.

For the data set of 179 observations used to derive the above predictive model (Jage and others, 2001), the standard deviation of the difference between observed and predicted values is about 50 mg/L. This deviation between predicted and observed values is the justification for suggesting sizing the system to generate alkalinity in excess of the anticipated need to offset incoming non-Mn acidity, especially if the system is intended to achieve regulatory compliance. Larger systems will provide an increased factor of safety, and are likely to operate successfully for a longer time prior to requiring major renovation.

[Figure 5](#) demonstrates that alkalinity generation rates vary considerably between systems. Two of the systems exhibited average alkalinity generation rates in excess of 300 mg/L and less than 2500 mg/day per square foot. In both of these systems, average residence times exceeded 300 hours. One southern West Virginia system exhibited an average alkalinity generation rate of approximately 7000 mg/day per square foot; this system had a relatively short residence time, a rich organic layer more

than one meter in thickness, and received AMD with pH's that are favorable to sulfate-reducing bacteria, in the 4-to-5 range. This system generated alkalinity most rapidly during the early years of its operation; during its third year, its performance declined considerably.

These data demonstrate Equation 9 may be used to provide design guidance, but does not provide precise predictions. Vertical-flow systems' performance exhibits considerable variation in the field, on a month-to-month basis as well as between locations ([Figure 6](#)). Building a system with a larger residence time will increase the probability of successful treatment.

For highly acidic AMD discharges, the above sizing method may generate an estimated residence time of several hundred hours. If area limitations prevent construction of such a large system, treatment may be provided as two or more successive vertical-flow cells separated by a settling pond. For example, considering the influent water chemistry represented by [Figure 3](#): a limestone residence time on the order of 1000 hours would be required in a single cell to generate 300 mg/L acidity, whereas two cells in series, each with a 30-hour residence time and separated by an settling pond, may be capable of generating a comparable amount of alkalinity. As a conservative design principle, we recommend that residence times of less than 15 hours should be avoided and longer residence times should be preferred. At low residence times (that is, at rapid rates of AMD movement through the vertical-flow system), the organic matter layer within the vertical flow system may begin to limit system performance. At very rapid rates of water movement, the permeability of the organic layer may become limiting ζ especially if Fe is being precipitated on its surface. Also, as the organic layer ages, its capacity to remove oxygen from the AMD will decline. Therefore, with all other things being equal, larger systems with slower residence times can be expected to maintain performance for longer periods than smaller systems with short residence times.

The residence time calculated with Equation 9 is an estimate of the time that the AMD should reside in the limestone layer to achieve desired results. In order to size the system, the residence time must be converted into a limestone layer volume (V_{ls}, expressed in cubic feet):

$$V_{ls} = \frac{8.02 Q t_r}{V_v} \quad (10)$$

where,

Q = influent flow (gallons per minute)

t_r = residence time in limestone (hours)

V_v = bulk void volume of limestone expressed as a decimal (e.g., 50% = 0.5)

A reasonable estimate of the bulk-void volume of 4-to-6 inch limestone is about 50%. For common unit-conversion factors, see [Table 1](#).

Adjusting Limestone Volume to Account for Loss over Time:

An additional volume of limestone should be added to compensate for limestone dissolution over the design life of the SAPS based on a method defined by Hedin and Watzlaf (1994) for ALDs. The additional volume of limestone needed (V_{ls+}, expressed as cubic feet) over the design size can be

calculated as:

$$V_{ls} = \frac{0.044 Q C T}{x} \quad (11)$$

where,

Q = influent flow (GPM)

C = predicted net alkalinity generation (mg/L)

T = design life (years)

x = CaCO₃ content of limestone, expressed as a decimal (e.g., 90% = 0.9)

This volume of limestone should be added to the amount needed to attain the design residence time (Table 2). By placing additional limestone in the vertical flow system, the design residence time will be maintained even as some limestone is dissolved by AMD moving through the system. Common practice is to design the limestone layer for 20- to 25-year lifetimes. High-calcium limestone should be used to construct the limestone layer; use of dolomitic limestones should be avoided. High-calcium limestone is more soluble than dolomitic limestone.

The Organic Layer

The organic layer is the most vulnerable of the major system elements and is critical to long-term performance. In addition to harboring sulfate-reducing bacteria, the organic layer removes dissolved oxygen and promotes reducing conditions necessary to prevent limestone armoring. The removal of dissolved oxygen, however, is directly related to water temperature and the AMD residence time in the organic matter. In order to ensure that the vertical-flow system performs well year-round and to prevent performance degradation due to limestone armoring, the organic layer must be sized adequately to ensure cold weather performance. Permeability is also a key property of the organic layer.

Well-weathered organic bark material has been used successfully in one high-residence-time Virginia system, but this system receives a relatively high-quality influent. Bark materials tend to be permeable, but they have a relatively low biochemical oxygen demand due to high proportions of large, woody debris that are not readily broken down by the bacteria. Other materials that are more easily processed by aerobic bacteria, such as composted manure or spent mushroom compost, should allow for shorter organic matter residence times given the greater bioavailability of the organic compounds in these materials. In practice, a variety of materials have been used successfully including well-decomposed wood mulch, spent mushroom compost, composted manure, and mixtures of composted materials with less-expensive organic sources such as rotting hay. Mixing organic-layer materials with limestone is not recommended, due to the potential for metal-hydroxide floc precipitation within the small pores of the mulch layer where flushing will not be effective.

For most systems, organic layer depths of 12 to 18 inches should be adequate. Deeper substrates can be problematic due to the low permeability of organic matter, especially as it begins to decompose. Shallower substrates should be avoided due to the risk of creating zones of preferential flow that would allow oxygenated water to reach the limestone layer. In designing systems with relatively rapid

movement of water through the organic layer due to exceptionally short residence times and/or large limestone-layer depths, the permeability of the organic-layer material should be tested.

Care should be used in installing the organic layer to assure that the material is well mixed and to assure uniform distribution and depth of material across the limestone-layer surface. Once the organic layer is in place, any activity causing compaction, such as walking or driving equipment on the surface of the system, should be avoided. Such activity may also result in the creation of zones of preferential flow. These areas will cause surface waters that are moving toward the drain to "short circuit" the system and decrease treatment effectiveness.

Drainage

The subsurface drainage system should be constructed from schedule 40 perforated PVC piping; piping diameter should be determined based on the design flow. Generally speaking, drainage diameters less than 6 inches should be avoided, due to the potential for metals precipitation and sediment accumulation within the drainage structure. Hole diameters should not be less than 1/2 inch, and 1 inch is preferred. The holes of tile drains, if used in vertical flow cells, should be enlarged. Adequately sized holes will help to ensure that plugging by floc precipitants does not occur. Typical layouts for the drain are 'T' or 'Y' shaped, and located in the lower 12 in of the limestone layer ([Figure 7](#)). Drains should be designed and oriented so as to promote full utilization of the limestone volume. The drains are joined to an effluent standpipe that is elevated to maintain a constant head of water above the organic substrate. The effluent should cascade into the adjacent settling pond in order to oxygenate the waters and promote the precipitation of the metals in solution.

A flushing system should also be included to maintain maximum treatment efficiency. This consists of a valved discharge port connected to the drainage network located at a level below the height of the effluent standpipe ([Figure 8](#)). When the valve is opened, the head of water in the vertical-flow system causes a rapid drawdown of the system, which removes the metal-hydroxide floc that can accumulate in the limestone layer. The flushing system outlet should discharge the floc into the settling pond to allow for the collection and removal of the precipitants. This drawdown process can require 10 to 15 minutes but should be continued until the discharge waters run clear.

A settling pond located after the vertical flow cell is crucial to effective treatment performance. For effective treatment prior to discharge, the settling pond is a necessity. The effluent of the vertical flow cell must undergo oxidation, pH adjustment, and subsequent precipitation of insoluble metal complexes before being discharged. The settling pond allows for these processes to take place in a controlled setting where the precipitates can be dredged and disposed of in a proper manner. Settling ponds should be large enough to allow for the accumulation of the precipitated metals with recommended residence times of at least 2.8 days (Skovran and Clouser, 1998).

Construction

Because Skovran and Clouser (1998) have produced a detailed guide to construction practice, only a small amount of construction guidance will be repeated here. Vertical-flow system construction requires the excavation of a basin, and a compacted clay or plastic liner to prevent seepage of untreated AMD into the groundwater. Side embankments may be constructed with 2:1 interior slopes and 3:1 exterior slopes with 8 - 10 ft top widths ([Figure 8](#)). Skovran and Clouser (1998) also recommend a minimum of 12 inches of freeboard above design high water to an emergency spillway in order to maintain system integrity.

Skovran and Clouser (1998) recommend considering public safety when designing the basin. Some

developers have chosen to encircle vertical-flow systems with chain link fences and post warning signs, in an effort to discourage uninvited visitors that might be attracted by the open waters. Configuring the basin to include a shallow-water bench area adjacent to the bank can enhance safety. Such a shallow bench separates the deep-water pool from bankside walking areas; in the event of accidental entry into the pool (e.g., someone falls in), the shallow bench will aid a quick exit. Depending on the AMD's acidity, the shallow bench may also become populated with cattails and other wetland vegetation, making entry to the deeper pool appear more difficult.

In long-term applications, the system basin should be situated so as to allow access by mechanical equipment, such as a back hoe or a small loader, to aid eventual system renewal.

Operation, Maintenance, and Renewal

Once the installation is complete, influent and effluent water-chemistry and flow monitoring should continue to allow assessment of system performance. Availability of adequate background data will enable informed decisions regarding maintenance if water treatment performance begins to deteriorate. Drainage systems should be flushed periodically; common practice is about one flush per month, but the frequency should be determined based on the rate of Al and Fe accumulation.

Both organic matter and limestone are consumed by vertical-flow system operation, so degradation of performance over time should be expected. When the operator determines that the time for renewal is at hand, the first step would be to drain the system and excavate the organic layer. Depending upon the degree of limestone armoring, the system operator may wish to either remove and replace the limestone, or add some additional limestone prior to re-installation of the organic layer. If substantial quantities of Fe-precipitate are deposited in the limestone layer due to organic layer deterioration, then the drainage system may also require replacement.

Table 1. Common conversion factors for use in vertical-flow system design.

Units	Equivalent units
1 gallon	0.134 cubic feet
1 gallon per minute	8.02 cubic feet per hour
1 cubic foot of 4-to-6 inch limestone	100 pounds (approximate)
1 pound CaCO ₃	454,000 mg of alkalinity (as CaCO ₃)

Table 2. Example Calculation

1. Determine design water quality and flow from field measurements: Fe concentration = 40 mg/l
Acidity = 200 mg/l as CaCO₃
Mn concentration = 25 mg /l
Flow = 10 gallons per minute
2. Calculate non-Mn acidity using Equation 8. 154.6 mg/l as CaCO₃
3. Determine design rate of alkalinity generation: Designer wishes to 250 mg/l alkalinity, as achieve a high probability of success, so the system is designed to CaCO₃ generate excess alkalinity.
4. Determine residence time necessary to achieve 250 mg/l of 270 hours alkalinity production, given the design water quality. Insert all parameters into equation 9; solve for residence time (Note that figure 3 was produced using influent data identical to this example).
5. Determine preliminary volume of 4-to-6 inch high-calcium 43,308 cubic feet limestone necessary to achieve desired residence time, using equation 10. (This estimate assumes bulk void volume = 50%).

6. Determine design lifetime of system. 20 years
7. Determine additional limestone needed to offset amount dissolved 2,444 cubic feet over design life, using Equation 11. (This estimate assumes CaCO₃ content of limestone = 90%).
8. Determine total volume of limestone needed (add 7 + 8). 45,752 cubic feet
9. Determine if project is worth further investigation:
 - Assuming a limestone layer of 4 feet and sloping sides, this project will require an area on the order of 12,000 square feet for the vertical flow cell alone.
 - If this amount of flat area is not available but some smaller areas separated by elevation differences, are available: recalculate the required area as two cells, each designed to produce 125 mg/l alkalinity or more per day, separated by a settling pond.
 - If either option looks feasible, involve a party experienced in passive treatment.

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J.J. Gusek
2002
Sulfate-reducing Bioreactor Design and Operating Issues

**SULFATE-REDUCING BIOREACTOR DESIGN AND OPERATING ISSUES:
IS THIS THE PASSIVE TREATMENT TECHNOLOGY FOR
YOUR MINE DRAINAGE?**

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ABSTRACT

There are basically two kinds of biological passive treatment cells for treating mine drainage. *Aerobic Cells* containing cattails and other plants are typically applicable to coal mine drainage where iron and manganese and mild acidity are problematic. *Anaerobic Cells* or *Sulfate-Reducing Bioreactors* are typically applicable to metal mine drainage with high acidity and a wide range of metals. Most passive treatment systems employ one or both of these cell types. The track record of aerobic cells in treating coal mine drainage is impressive, especially back in the eastern coalfields. Sulfate-reducing bioreactors have tremendous potential at metal mines and coal mines but have not seen as wide an application.

This paper presents the advantages of sulfate-reducing bioreactors in treating mine drainage, including the ability to work in cold, high altitude environments; handle high flow rates of mildly affected ARD in moderate acreage footprints; treat low pH acid drainage with a wide range of metals and anions including uranium, selenium, and sulfate; accept acid drainage-containing dissolved aluminum without clogging with hydroxide sludge; have life-cycle costs on the order of \$0.50 per thousand gallons; and be integrated into "semi-passive" systems that might be powered by liquid organic wastes.

Sulfate reducing bioreactors might not be applicable in every abandoned mine situation. A phased design program of laboratory, bench, and pilot scale testing has been shown to increase the likelihood of a successful design.

Additional Key Words: Constructed wetlands, acid mine drainage, heavy metals, sulfate reduction

INTRODUCTION

It has been over 20 years since the pioneering work of a group of researchers at Wright State University documented water quality improvements in a natural *Sphagnum* bog in Ohio that was receiving low pH, metal laden water (Huntsman, et al., 1978). Independently, a group at West Virginia University found similar results at the Tub Run Bog (Lang, et al., 1982). Subsequently, researchers, practitioners, and engineers focused on developing the promising technology of using “constructed wetlands” to treat acid mine drainage (AMD) or acid rock drainage (ARD). But the term “wetland,” besides carrying legal and regulatory baggage, does not quite describe structures like “anoxic limestone drains” or “successive alkalinity producing systems;” hence, the term “passive treatment” was coined.

The design of passive treatment systems basically entails the selection of treatment “modules” appropriate to the geochemistry of the mine drainage. As shown in Figure 1, there are two geochemical “zones” in a natural wetland ecosystem. The lower, oxygen-depleted zone is where sulfate-reducing bacteria thrive. The focus of this paper will be the design of passive treatment modules that capitalize on the geochemical reactions typically found in the anaerobic zone of natural systems.

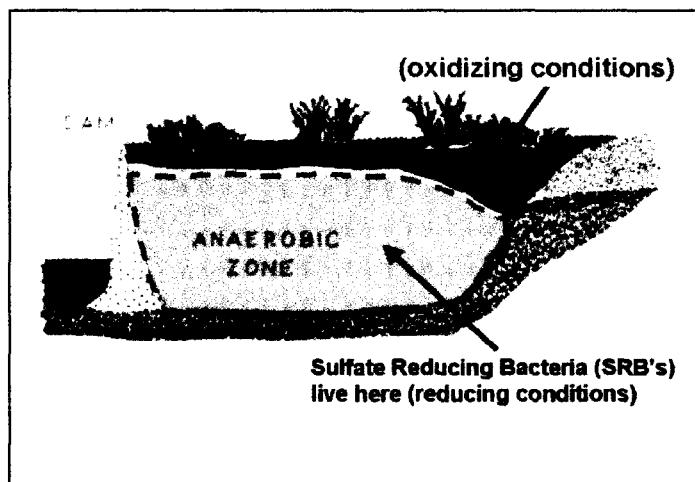


Figure 1. Typical Natural Wetland Geochemical Zones

Definition of Passive Treatment

There are many technologies for treating AMD/ARD. To properly focus the discussion, the following definition of passive treatment is proposed:

Passive treatment is a process of sequentially removing metals and/or acidity in a natural-looking, man-made bio-system that capitalizes on ecological and geochemical reactions. The process requires no power and no chemicals after construction and lasts for decades with minimal human help.

It is a *sequential* process because no single treatment cell type works in every situation or with every AMD/ARD geochemistry. It is an *ecological/geochemical* process because most of the reactions (with the exception of limestone dissolution) that occur in passive treatment systems are biologically assisted. Lastly, it is a *removal* process because the system must involve the filtration or immobilization of the metal precipitates that are formed. Otherwise, they would be flushed out of the system, and the degree of water quality improvement would be compromised.

A truly passive system should also function for many years, without a major retrofit to replenish construction materials, and be able to function without using electrical power. Benning and Ott (1997) described a volunteer passive system outside of an abandoned lead-zinc mine in Ireland that has apparently been functioning unattended for over 120 years. Ideally, a passive treatment system should be designed to last for at least several decades.

METAL REMOVAL AND OTHER BIO-GEOCHEMICAL MECHANISMS IN PASSIVE TREATMENT SYSTEMS

Many physical, chemical, and biological mechanisms are known to occur within passive treatment systems to reduce the metal concentrations and neutralize the acidity of the incoming flow streams. Notable mechanisms include:

- Sulfide and carbonate precipitation catalyzed by sulfate-reducing bacteria (SRB) in anaerobic zones
- Hydroxide and oxide precipitation catalyzed by bacteria in aerobic zones
- Filtering of suspended material
- Metal uptake into live roots and leaves
- Adsorption and exchange with plant, soil, and other biological materials.

Remarkably, some studies have shown that plant uptake does not contribute significantly to water quality improvements in passive treatment systems (Wildeman, et al., 1993). However, plants can replenish systems with organic material and add aesthetic appeal. In aerobic systems, plant-assisted reactions appear to aid overall metal removal performance, perhaps by increasing oxygen and hydroxide concentrations in the surrounding water through photosynthesis-related reactions and respiration in the plant root zone. Plants also appear to provide attachment sites for oxidizing bacteria/algae. Research has shown that microbial processes are a dominant removal mechanism in passive treatment systems (Wildeman, et al., 1993). One anonymous researcher considered a passive treatment system as a “bioreactor with a green toupee,” referring to the substrate where most of the bioreactions occur and the collection of plants that grow on top of the treatment cells.

Sulfate Reducing Bioreactors

Sulfate reduction has been shown to effectively treat AMD/ARD containing dissolved heavy metals, including aluminum, in a variety of situations. The chemical reactions are facilitated by the bacteria *desulfovibrio* in sulfate-reducing bioreactors as shown in Figure 2 in schematic form and the photo in Figure 3.

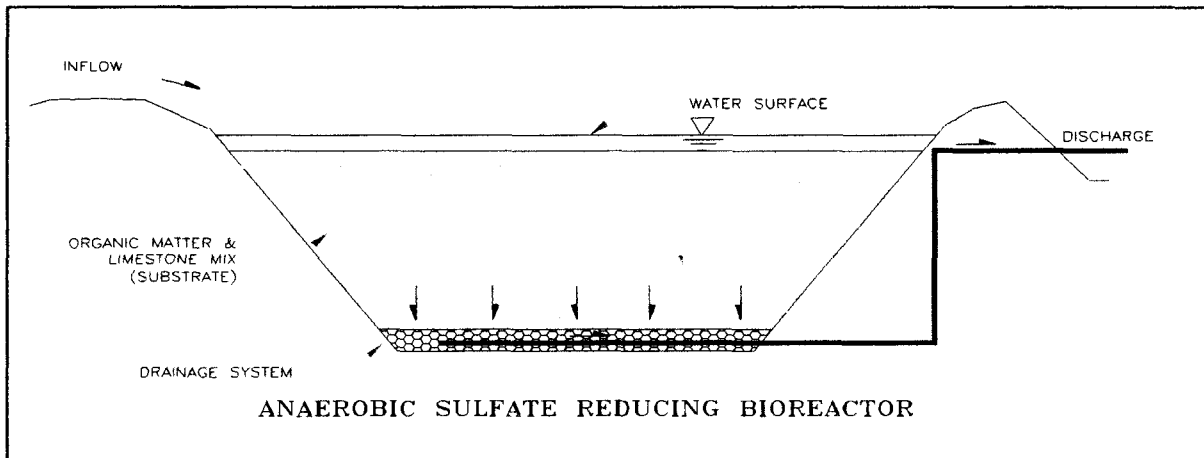


Figure 2. Sulfate-Reducing Bioreactor Schematic

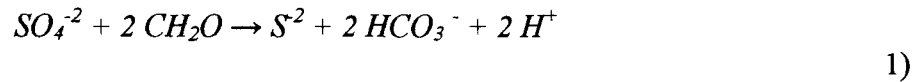


Figure 3. A Typical Sulfate-Reducing Bioreactor

The sulfate-reducing bacterial reactions (equation 1) involve the generation of:

- Sulfide ion (S^{2-}), which combines with dissolved metals to precipitate sulfides (equation 2)
- Bicarbonate (HCO_3^-), which has been shown to raise the pH of the effluent

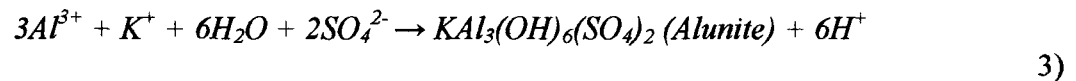
The sulfate reducing bacteria produce sulfide ion and bicarbonate in accordance with the following reaction (Wildeman, et al., 1993):



The dissolved sulfide ion precipitates metals as sulfides, essentially reversing the reactions that occurred to produce AMD/ARD. For example, the following reaction occurs for dissolved zinc, forming amorphous zinc sulfide (ZnS):



Suspected geochemical behavior of aluminum in sulfate reducing bioreactors has just recently been documented (Thomas and Romanek, 2002). It is suspected that insoluble aluminum sulfate forms in the reducing environments found in sulfate-reducing bioreactors, perhaps in accordance with the following reaction which is one of many possible:



The key conditions for SRB health are a pH of 5.0 (maintained by the SRB itself through the bicarbonate reaction and/or the presence of limestone sand), the presence of a source of sulfate (typically from the AMD/ARD), and organic matter ([CH₂O] from the substrate). Sulfate-reducing bioreactors have been successful at substantially reducing metal concentrations and favorably adjusting pH of metal mine drainages.

FLOW CHART FOR PASSIVE TREATMENT SYSTEM DESIGN

In the late 1980s, the design methods for aerobic passive treatment cells for iron removal were still under development. Brodie (1991) sorted out the empirical relationships in a milestone design flow chart that provided the foundation for a more comprehensive design flow chart subsequently developed by Hedin and Nairn at the former U.S. Bureau of Mines as shown in Figure 4.

This figure, in one form or another, continues to guide engineers and practitioners in the passive treatment cell design process. It has been modified by the author to include the passive treatment of heavy metal-bearing AMD/ARD based on observations since 1988. The sulfate-reducing bioreactor as shown reflects where this particular technology fits in the design philosophy. Although the technology is well suited for AMD/ARD with net acidity and/or heavy metals, it can also be effectively applied to net alkaline water sources as indicated by the arrow drawn from the settling pond on the left hand side of the flow chart.

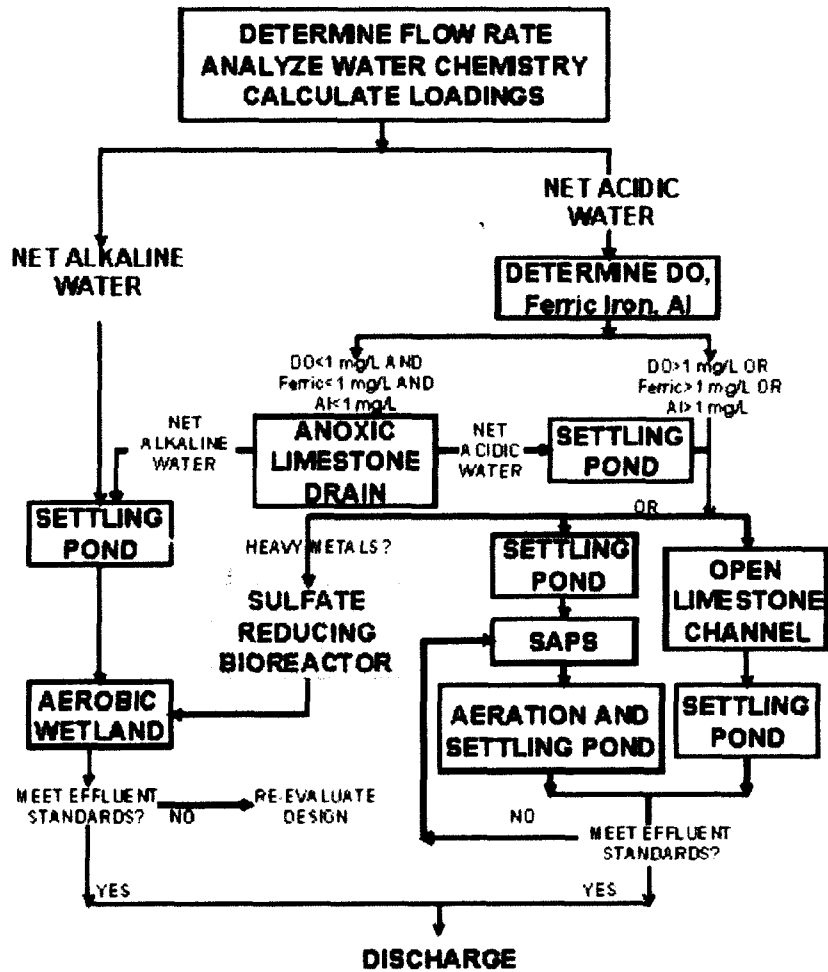


Figure 4. Flow Chart for Selecting a Passive AMD Treatment System Based on Water Chemistry and Flow (Adapted from Hedin, et al., 1994).

PHASED DESIGN PROTOCOL

There is no “cookbook” design manual for passive treatment systems although the design flow chart above is a safe starting point. A phased approach design project is recommended; it typically begins in the laboratory with static tests, graduating to final testing phases (bench and pilot) performed at the site on the actual AMD/ARD. Bench scale testing will determine if the treatment technology is a viable solution for the AMD/ARD and will narrow initial design variables for the field pilot. A proper bench scale test will certainly reduce the duration of the more costly field pilot test. Field pilot test duration can range from days, to months, to years, depending on the nature of the technology. Depending on the nature of the equipment and personnel needed, significant costs may be incurred during the field pilot tests – about \$500 to \$1,000 per week, mostly for sampling and analysis. Compare this to \$5,000-\$10,000 per week

for active treatment pilot tests. More detailed descriptions of laboratory, bench, and pilot tests are provided in Gusek (2001).

ADVANTAGES OF SULFATE-REDUCING BIOREACTORS

As shown in Figure 4, sulfate-reducing bioreactors can be applied in a number of different AMD/ARD situations. While most passive treatment systems (both aerobic zone and anaerobic zone types) offer simplicity of design and operation and economic advantages over active/chemical treatment, sulfate-reducing bioreactors have advantages worth considering.

- No aluminum plugging
- Can easily handle low flow net acidic water or high flow net alkaline water
- Uses waste organic materials
- Resilient to loading and climate variations
- Consumes sulfate; capable of treating selenium and uranium
- Generates more net alkalinity in effluent
- Burial to minimize vandalism
- Opportunities for community involvement in organic procurement
- Might be able to construct them in abandoned underground mines

Brief discussions of these issues follow.

No Aluminum Plugging

When AMD/ARD attacks clay-bearing formations at mining sites, significant amounts of dissolved aluminum can be created. The geochemistry of aluminum is complex, and this can cause problems in passive treatment systems. The formation of the mineral gibbsite $[Al(OH)_3]$ is especially problematic as it is a gelatinous solid. Gibbsite tends to form in limestone-dominated passive treatment cells, and the sludge tends to plug the void spaces between the limestone rock, becoming a major maintenance problem. While the precise mechanisms are just beginning to be understood (Thomas and Romanek, 2002), the precipitation of gibbsite is avoided in SRB cells. It is suspected that unidentified alternative aluminum compounds form in the SRB cells instead of gibbsite, and these compounds are less prone to plugging. Several case histories of SRB passive treatment projects that involved treating ARD with high aluminum concentrations are provided in Gusek and Wildeman (2002)

Use of Waste Materials in Construction

Organic materials are a key component in the formulation of the substrate of sulfate-reducing bioreactors. Often these materials are considered waste materials and can be obtained for little or no purchase cost. The only expense incurred might be in their transport to the treatment site. If the site is in a remote forest environment, some of the materials such as wood chips and sawdust might be generated onsite or from local sources. A short list of organic waste materials, both solid and liquid, that might be candidates for use in a sulfate-reducing bioreactor is provided below. The list is not necessarily all inclusive as specialty wastes unique to different locales might be available.

- Wood chips
- Sawdust
- Yard waste
- Mushroom compost
- Animal manure
- Partially treated sewage?
- Hay and straw (spoiled)
- Cardboard?
- Waste alcohols including antifreeze
- Waste dairy products
- Sugar cane processing residue (Bagasse)

Using liquid organic wastes poses a specific opportunity and challenge. These materials are typically very biodegradable and as such are considered “candy” to sulfate-reducing bacteria. Thus, they are consumed quickly and need to be replenished on a nearly continual basis. This is not consistent with the strict definition of passive treatment cited earlier. However, since these materials might be stored in tanks or fed continuously from offsite sources through pipelines, systems using these waste organic sources would be considered “semi-passive” in nature. Such cells are often called “enhanced sulfate-reducing bioreactors” due to the boost provided by the liquid organic material. When alcohol is the chosen enhancer, the technique has sometimes been called “bugs on booze.”

Resilient to Loading and Climate Variations

If properly designed, sulfate-reducing bioreactors can be resilient to metal-loading variations. Pilot scale tests are the best venue for establishing the expected operating ranges of flow and metal concentrations and the reactions of the SRB cells to those varying conditions. For example, a pilot SRB cell at a lead mine in Missouri was sized for 25 gpm. Once steady state operation was observed for many months, the flow was increased to nearly double the design rate. The SRB cell began to show evidence of stress (i.e., decreased metal removal efficiency) after several months of exposure to the higher flow (Gusek, et al., 1998). Not all SRB cells might be this resilient, but this observation allowed engineers to include a significant factor of safety in the design of the full-scale system (1,200 gpm capacity) at this site.

Low temperature operation is a major concern at some sites, especially in the mountainous states in the west and Appalachia. Pilot cell data at the Ferris Haggarty Copper Mine/Osceola Tunnel Site in Wyoming at elevation 9,500 feet suggests that sulfate reduction rates decline in cold weather, but the decrease is not significant enough to render the design concept untenable. At this site, the typical water temperature is about 4°C. Winter operational data revealed that the cell continued to function at temperatures less than 1°C, and the sulfate reduction rate was estimated to be about 0.24 moles per day per cubic meter (m/d/m³) (Gusek, 2000). Compared to the benchmark design value of 0.3 m/d/m³, this constitutes a 20 percent decrease.

Sulfate-Reducing Bioreactors Consume Sulfate; Selenium and Uranium Reduced

Sulfate is a component of AMD/ARD that may be receiving more regulatory attention. It contributes to the total dissolved solids (TDS) concentration. But unlike other TDS constituents such as sodium, chlorine, and calcium, it is not conservative and can be mitigated in sulfate-reducing bioreactors. No other passive treatment technique has this capability as its primary function. Some sulfate reduction is typically observed in Successive Alkalinity Producing

Systems (SAPS) (see Kepler and McCleary, 1994), but their primary function is to add alkalinity through limestone dissolution.

While sulfate-reducing bioreactors are naturally efficient at consuming sulfate, the geochemical conditions generated in a typical cell are also conducive to reducing selenium from the dissolved state to elemental selenium; this is facilitated by selenium-reducing bacteria. They are also effective in reducing uranium from the oxidized state to form insoluble uranium oxide similar to the way that some natural uranium deposits formed.

Burial to Minimize Vandalism

Any passive treatment system might be a target for vandalism. Because neither plants nor air are required for the sulfate-reducing bioreactors to function, they can be buried beneath a veneer of rock and soil provided that the feed water plumbing to the cell is not compromised. Settlement of the organic substrate needs to be considered in the design if burial is being considered. However, most organic substrate designs typically include a large component of wood chips or sawdust, which do not readily compress under minor surcharge loads developed by soil/rock covers. This aspect of the design should ideally be evaluated at the pilot stage of the design effort.

Underground In-Mine Treatment Systems

As stated above, one of the beauties of SRB systems is that they do not require plants to operate. All that is needed is a carbon source and an SRB arranged in a manner that encourages bacterial growth in concert with managed loading of AMD/ARD. In areas where land surface favorable to passive treatment system construction is at a premium due to steep terrain or the encroachment of civilization, building passive treatment systems in abandoned underground mine voids (using the mine void itself as the containment "vessel") is an attractive possibility that has been realized in only one study at a metal mine in Montana (Canty, 1999).

Two challenges to overcome to implement this technology include the placement of large volumes of solid organic matter into mine voids through boreholes and the procurement of inexpensive organic material like forestry or paper waste and animal manure (SRB inoculum). The introduction of animal manure (even in small amounts) into ground water (i.e., a mine pool) will be a regulatory hurdle that may prove to be difficult to surmount. Carefully controlled field tests in small mines will probably be required.

Low Flow Net Acidic Water or High Flow Net Alkaline Water

At a given flow rate, the footprint of a sulfate-reducing bioreactor is governed by the mineral acidity of the AMD/ARD. The higher the acidity, the larger the surface area is required per unit of flow. The land area available for the system may be limited, especially for high flows of net alkaline AMD/ARD. In this situation, the surface area of the SRB cell might be as small as 10 square feet per gpm of flow. Thus, a net alkaline flow of 2,000 gpm might require as little as 20,000 square feet or about half an acre of cell. Cell depth will be a function of metal load.

Conversely, a very acidic AMD/ARD source might require a similar area to treat a significantly less flow rate. For example, a flow of only 30 gpm of AMD with over 2,000 mg/L of acidity would require nearly 3 acres of surface area. However, there are no other technologies capable of passively treating AMD/ARD with this aggressive a chemistry.

Added Net Alkalinity in Effluent

Sulfate-reducing bioreactors are typically sized to deliver treated water with low concentrations of metals and a near neutral pH. However, experience has shown that SRB cell effluents typically contain excess alkalinity at concentrations above those expected from SAPS units or anoxic limestone drains. This excess alkalinity is therefore available to ameliorate acidity contributions that might be impacting the receiving stream far removed from the original passive treatment site.

New Opportunities for Community Involvement

The construction of passive treatment systems is an ideal way to make the most of community volunteerism. The transplanting of wetland vegetation is the most common activity in which volunteers can become involved with passive treatment projects. However, the collecting of organic materials for sulfate-reducing bioreactor substrate opens an entirely new opportunity for local community organizations to release pent-up volunteerism. Some pet owners are often hard pressed to find useful and environmentally sound ways to dispose of significant amounts of manure (e.g., horse). Homeowners could divert tree trimmings or yard waste away from the local landfill and into a community stockpile of wood waste to be mulched (but not composted) and used in a nearby sulfate-reducing bioreactor. Farmers would have a place to dispose of moldy hay. Community events similar to paper drives could be used to collect materials in advance of a project. This not only lowers the cost of the project but also provides additional community buy-in.

SULFATE-REDUCING BIOREACTOR DESIGN EXAMPLES

Design Example No. 1

This is a hypothetical abandoned underground coal mine in Appalachia with a relatively small mine pool. The site is adjacent to a fresh water lake. The flow varies through the year, but the AMD chemistry is fairly constant. SAPS had been considered at this site but rejected due to the elevated aluminum concentration. Pertinent design parameters are listed below.

- 67 gpm peak flow
- pH = 2.5
- Fe = 152 mg/L (ferric iron)
- Aluminum = 30 mg/L
- Acidity = 500 mg/L
- 990 moles of Fe per day

The hypothetical passive treatment system will include two sulfate-reducing bioreactors (each treating 50 percent of the flow) to raise the pH, produce net alkalinity, to remove nearly 100 percent of the aluminum and 95 percent of the iron. The system would comprised the following components:

- 1.7 acres of SRB cell 3 feet deep
- 0.25 acres of aerobic polishing cell

The costs of developing this design from initial concept to complete construction include:

- \$30,000 to \$50,000 for bench and pilot studies
- \$315,00 design and construction (assuming no donated materials or labor)

The 8,250 cubic yards of organic substrate originally installed would require replacement every 20 to 30 years. The substrate typically comprises about 33 percent of the construction cost. This would be about \$110,000 or less depending on the availability of local materials and in-kind donations. This and other maintenance costs are summarized on an annual basis in the table below. Some of these costs might be minimized through volunteer labor and other contributions.

Maintenance Item	Annual Cost
Replace Substrate	\$3,569
Dispose Substrate (20% of replacement cost.)	\$714
Weekly inspection & pipe clean?	\$5,000
Flushing for aluminum buildup	\$0
Sampling/lab costs lump sum	\$15,000
	\$24,283

The life cycle cost of this treatment (includes capital and operating cost) is about \$0.70 per thousand gallons treated.

Design Example No. 2

This is another hypothetical abandoned underground coal mine in Appalachia but with a relatively large mine pool covering over 100,000 acres. The site contributes nearly 50 percent of the metal load to a nearby river. The flow is relatively steady through the year, and the AMD chemistry is constant as well. The site has only 6 acres available for construction of a main treatment system, but there are no restrictions on effluent polishing. This is a major project due to the flow rate. Pertinent system design parameters are listed below.

- 3,000 gpm from a deep mine pool
- Sulfate = 1000 mg/L (50 effluent goal)
- pH = 5.5
- Fe⁺² = 150 mg/L
- Al = 2 mg/l

- Mn = 2.7 mg/L (0.05 effluent goal)
- Acidity = 50 mg/L (“Hot Acidity”)

The 6-acre restriction eliminates a standard sulfate-reducing bioreactor. However, an enhanced sulfate-reducing bioreactor (ESRB) is feasible due to the steady availability of a waste alcohol product and other factors. The enhancement allows the footprint of the ESRB cell to shrink to easily fit in the space available. The ESRB effluent will have a neutral pH and some excess alkalinity. However, it will also have elevated biological oxygen demand (BOD) and manganese, which require further polishing. Key features of this hypothetical system include:

- 4 acres of enhanced sulfate-reducing bioreactor cell 6 feet deep
- 9 acres of aerobic polishing cell (for Mn and BOD treatment)

The costs of developing this design from initial concept to complete construction include:

- \$200,000 for bench and pilot studies
- \$1.36MM design and construction

The operating cost of the enhanced sulfate-reducing bioreactor (including paying \$2.00 per gallon for the alcohol) is \$674,000 per year or \$0.43 per 1000 gallon treated. The system effluent would meet drinking water standards. To be conservative, the above cost assumes that the substrate in the ESRB be replaced every 20 to 30 years due to metal sulfide precipitate buildup.

Design Example No. 3 - Do SRBs Need More Room?

This design example compares the area requirements for using a standard aerobic wetland and a standard sulfate-reducing bioreactor to treat a relatively large net alkaline flow. The design assumptions are listed below.

- 3,000 gpm from a deep mine pool
- pH = 6.5
- Fe+2 = 50 mg/L (817,560 grams/day or 14,638 moles per day)
- Net alkaline
- No manganese
- 10 acres available for main treatment cells

If an aerobic wetland dominated by cattails and other vegetation was designed on the standard assumption of 11 grams/day per square meter of iron loading criteria (which was established by U.S. Bureau of Mines researchers), approximately 18 acres of wetland habitat would be needed.

A sulfate-reducing bioreactor with an identical treatment capacity would cover 8 acres (probably split into four 2-acre cells plumbed in parallel). The cells would be 7.5 feet deep, and the AMD/ARD would enter them at the bottom and exit at the top. This upflow configuration allows the top of the cell to function as a primary dissolved oxygen polishing cell. The remaining

2 acres available would be fitted with a final aerobic polishing cell to complete the facility. In this situation, both cell types would work geochemically, but only one – the sulfate-reducing bioreactor – would be feasible.

SUMMARY

Sulfate-reducing bioreactors are not the only type of passive treatment technique available to the design engineer, and they are not applicable in every situation. However, they can handle a wide variety of flows and AMD/ARD chemistries in hostile cold climates, and they can treat aluminum-bearing AMD/ARD without plugging. Furthermore, they can generate excess alkalinity in their effluent that further enhances the quality of the receiving stream.

Sulfate-reducing bioreactors typically require large amounts of organic materials that are usually considered waste. Enhanced SRB cells can consume liquid organic wastes like antifreeze or cheese whey.

While not readily practiced, it may be feasible to build them in mine voids to provide in situ treatment at sites with limited land area.

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Pamela Milavec and D. Seibert

2002

**Pennsylvania's Efforts to Address Operation, Maintenance and
Replacement of AMD Passive Treatment Systems**

PENNSYLVANIA'S EFFORTS TO ADDRESS OPERATION, MAINTENANCE AND REPLACEMENT OF AMD PASSIVE TREATMENT SYSTEMS

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ABSTRACT

An increasing number of watershed groups, as well as many Federal, State and local agencies, have become active in watershed restoration over the past several years. As a result, a large number of restoration projects are being funded and constructed. In Pennsylvania, a total of nearly \$93 million of public money has been spent on all types of watershed restoration projects since 1988. A portion of this funding has gone to construct 153 AMD passive treatment systems statewide. Funds have come from a variety of sources, including the Office of Surface Mining's Title IV program, the Natural Resources Conservation Service's (NRCS) PL-566 program, Pennsylvania's Growing Greener program and the Environmental Protection Agency's 319 Non-Point Source program. Water quality and aquatic habitat improvements are occurring as these projects are implemented. The need for long-term operation, maintenance and replacement (O, M & R) has been increasingly recognized as a requirement to ensure the success of watershed restoration projects. The failure to maintain the systems being constructed could have detrimental impacts to watersheds that are beginning to support an increasing number of stream uses. As a result of growing concern over this issue, the PA Department of Environmental Protection (DEP) established a workgroup to provide recommendations to address this need. The workgroup consisted of individuals from Federal, State and local governments, as well as private consultants and watershed group officials. All had extensive experience in the operation and maintenance of watershed restoration projects, both mining and non-mining related. Recommendations were finalized by late 2001.

The NRCS and DEP have taken a lead role in implementation of these recommendations, including the development of maintenance plans and agreements, working with local watershed groups to provide routine maintenance and trouble-shooting to solve problems that arise. Their experiences are providing a greater understanding of the efforts needed to keep systems functioning properly.

INTRODUCTION

In Pennsylvania, watershed groups and various government agencies started constructing passive treatment systems to treat abandoned mine drainage (AMD) in the early 1990's. The design of these systems has evolved from simple, aerobic wetlands to complex vertical flow alkalinity generating systems with mechanisms to flush accumulated metals. While the design improvements have resulted in the ability to treat highly acidic discharges, the resulting systems have required significantly more effort to keep them operating effectively. Early vertical flow systems that did not have adequate flushing mechanisms have started to fail due to plugging by metals. Additional problems have surfaced at older systems, including leaks, short-circuiting

and metals accumulation. All these experiences have pointed to the need to address long-term operation, maintenance and replacement (O, M & R) of AMD passive treatment systems.

The need to address O, M & R became even more pressing as additional funding was made available to build these types of systems. Early on, funds were provided by the EPA 319 Non-Point Source program, the Natural Resources Conservation Service (NRCS) Rural Abandoned Mine Program and P.L. 566 program and the Federal Office of Surface Mining's Ten Percent Set Aside and Appalachian Clean Streams Initiative (ACSI) programs. These funds continue to increase, while significant additional funding has surfaced with the establishment of Pennsylvania's Growing Greener program in 1999.

In June 2000, State Representative Sam Smith provided remarks at a statewide AMD conference that emphasized the need to address O, M & R in watershed restoration work. Many others working in the AMD treatment field were recognizing the same need. As a result, the PA Department of Environmental Protection (DEP) established a workgroup in early 2001 to develop recommendations to address this problem. The workgroup met throughout 2001 and finalized recommendations to DEP Secretary David Hess in November, 2001. These recommendations are provided in Attachment A. Since that time, much effort has gone into implementation of the recommendations. The DEP and NRCS have been leaders in that effort, along with several strong watershed groups and knowledgeable consultants.

IMPLEMENTATION

A major focus of implementation of the workgroup's recommendations has been the educational aspect. Members of the workgroup spoke at various conferences and Growing Greener training workshops in order to develop an awareness of the need to address O, M & R. Also, several changes were implemented in the Growing Greener program (the single most significant funding source) as a result of the recommendations. They included: developing an O, M & R fact sheet, providing detailed information in the application packets about the need to address O, M & R in the application, changing project score sheets to emphasize the need for O, M & R on implementation projects, and requiring the development of an O, M & R plan for all construction projects. In addition, a separate funding category has been developed to address funding of O, M & R projects with significant costs, starting with the 2003 round. The State Legislature passed Legislation in late June that continues Growing Greener through 2012 and provides a permanent funding source for the program.

The development of O, M & R plans has become a major focal point for projects constructed by the NRCS, under their P. L. 566 program, and the DEP's Bureau of Abandoned Mine Reclamation (BAMR), which uses OSM and Growing Greener funds to construct treatment facilities. These plans emphasize the partnerships with local watershed groups that are needed to provide for necessary O, M & R. O, M & R plans are developed for all NRCS projects and all new BAMR projects. The NRCS requires local sponsors in counties where the projects are located to accept the responsibility for all O, M & R needs. Operation and maintenance agreements and plans are prepared for the sponsors. NRCS staff provides consultation and technical input when significant maintenance is needed. BAMR looks upon the local groups to provide for routine monitoring, operation and minor maintenance requirements. Training is provided to the local groups where needed. BAMR is responsible for more significant maintenance needs and for eventual system replacement.

A major issue with regard to O, M & R is monitoring, particularly water sampling and laboratory analysis. Monitoring of the treatment system efficiency is very important – it provides feedback for future design improvements and signals when systems are not operating properly and may need maintenance. Typically, local groups and BAMR staff collect the samples and DEP's laboratory provides the analysis. This has proven to be a significant portion of the expenses involved with O, M & R. Determining how best to deal with this cost is an ongoing issue within DEP that has yet to be resolved. The DEP has recently convened a small workgroup to address this.

TECHNICAL ISSUES

A number of difficult technical issues have arisen with regard to the long-term operational efficiency of AMD passive treatment systems. The most complex issue deals with metals precipitation within the systems, particularly vertical flow systems that treat net acid water. Vertical flow systems typically consist of a layer of standing water over organic material (usually mushroom compost), which is underlain by limestone with a pipe collection system below the limestone. In theory, vertical flow systems are expected to keep ferrous iron in the ferrous state and to reduce existing ferric iron to a ferrous state as a result of a lack of oxygen in the system (the compost layer strips oxygen present in the water as a result of the biological oxygen demand of the compost). Ferrous iron is expected to pass through the limestone and precipitate in a subsequent settling basin. Aluminum, which comes out of solution as the pH increases, whether or not oxygen is present, is expected to precipitate within the compost and/or limestone layer. Flushing is expected to remove precipitated aluminum. However, field evidence indicates that most systems retain some iron within the limestone. In a few cases, iron has precipitated on top of the compost layer, causing the system to plug. While flushing these systems provides visual evidence of both iron and aluminum removal from the systems, a recent study has indicated that only a small percentage of retained metals is being flushed from the system in two systems studied (Watzlaf, 2001). The long-term implication of this is unknown, but efforts are underway to determine the best way to design the flushing systems to maximize removal from the limestone.

A less frequent problem occurs when ferric iron precipitates on top of the compost in vertical flow systems, as the pH starts to increase. When this occurs, it eventually reduces the permeability of the compost until water cannot flow vertically through the system. Since the solubility of iron is pH dependent and precipitation occurs more rapidly as the pH increases (Hem, 1992), the pH of the raw water that is being treated must be carefully considered when designing systems with high iron levels. Creating larger precipitation ponds and wetlands before the vertical flow systems can reduce the amount of ferric iron reaching the vertical flow system.

Accumulation of aluminum in the top 6 inches of the rock layer in vertical flow systems can create hydraulic conductivity problems within the limestone. As mentioned earlier, oxygen is not needed to precipitate aluminum - there only needs to be an increase in pH to above 4.5 (Hem, 1992) for precipitation to occur. In many systems, this pH increase occurs in the upper areas of the limestone rock column, or even within the compost. The initial precipitation of aluminum creates a very loose, jelly-like precipitate ($2\text{Al}(\text{OH})_3$) that is easily dislodged and flushed from the rock. This precipitate is easily flushed from the system when aggressive flushing systems are initially designed in the system. Frequent flushing is recommended, at least quarterly, to keep the aluminum purged from the system. Field observations indicate that if the

aluminum is allowed to accumulate in the rock to point where hydraulic conductivity is reduced, the flushing of aluminum becomes more difficult. Also, aluminum precipitate seems to harden and take on a paste consistency with time and becomes harder to flush.

Other problems encountered with vertical flow systems include short-circuiting caused by the development of preferential flow paths through the compost layer. This has especially been evident on several systems where the compost was washed out immediately below the influent point to the system. Dispersing the inflow through a manifold rather than at a single, point-source location seems to help this. The configuration of the piping system underlying the limestone rock can also impact short-circuiting through the system. Long narrow systems that have continuous pipes running along the longitudinal axis of the system seem to short circuit through the piping system. This apparently results from the water entering the piping near the influent end of the system and traveling through the piping rather than through the limestone. Segmenting can alleviate this, or zoning the piping system by designing incremental breaks in the pipes to force the flow of water into the limestone (Danehy et al., 2002). Consideration of a system with a lower length to width ratio during the design phase also may be important in reducing short-circuiting.

The most frequently used source of organic material in vertical flow wetlands is spent mushroom compost. The function of the compost is to reduce ferric iron to ferrous iron and provide a medium for biological activity. When new systems are first put into service the mushroom compost can create very high biological oxygen demands (BOD) on the stream receiving the treated water. If aquatic life is present in the stream at the time the system goes on line, the BOD may kill much of the aquatic life present in the stream. To manage this potential problem, it is best to install a valve on the inflow pipe to the system and limit the amount of water entering the system. This allows for a slow flushing of the BOD out of the system and prevents an aquatic kill on the receiving stream.

OVEN RUN CASE STUDY

Stony Creek is a historically AMD impacted watershed located primarily in Somerset County, PA. The first major source of AMD to Stony Creek was a tributary known as Oven Run. The Oven Run AMD Abatement Project was developed under an NRCS PL-566 plan, the first in the country approved to address AMD. Six project areas were identified for abatement in the plan. Five of the six project sites required passive treatment using vertical flow systems. With completion of the first five projects by the fall of 1999, the Stony Creek turned from net acidic to net alkaline for a distance of 22 miles. The project has been very successful and has restored a recreational fishery in a stream long considered to be dead. The amazing success of this project has occurred even though three of these systems have had O & M related problems, which will be discussed below. Although the Somerset County Commissioners signed an agreement to be the responsible O & M entity under the PL-566 Plan, both BAMR and the NRCS have taken the lead role in addressing the technical problems that have arisen.

Oven Run Site A, the sixth and final site to be constructed, was just completed in the spring of 2002 using NRCS and Growing Greener funds. It consists of a passive treatment system that incorporates many design features developed as a result of lessons learned from the sites constructed earlier. Specifically, aerobic wetlands and limestone filter dams were used to remove as much ferric iron as possible prior to the vertical flow wetland. Also, an aggressive flushing system was constructed. Initial indications are that this site is functioning as designed.

Routing water sampling of the system is planned starting in the fall of 2002, after the system has stabilized.

Oven Run Site B was completed in 1999 by BAMR, using OSM ACSI and Ten Percent Set Aside funds. BAMR has continued to provide all monitoring, operation and maintenance at this site, although turning routine operation and maintenance to the Somerset Conservation District is a future possibility. Site B has a design flow of 350 gpm, although the system has successfully treated flows as high as 450 gpm. The influent has acidity between 500 and 600 mg/l, total iron between 55 and 85 mg/l and aluminum between 35 and 45 mg/l. The system consists of a deep mine drainage collection trench, a vertical flow wetland, settling pond, second vertical flow wetland and second settling pond. Until spring of 2000, the system effluent was net alkaline, with very low metals concentrations. After flows increased in the spring of 2000, effluent quality degraded to the point that net acid water was being discharged with a pH in the low 4's and elevated iron and aluminum. This situation continued, even after flows subsided. Site inspectors had observed an opening in the compost directly below the point of influent discharge into the first vertical flow system. BAMR's construction crew was brought in to construct an inflow manifold system to spread influent over a larger area and prevent the development of preferential flow paths through the compost. The expected water quality improvements did not occur, although this vertical flow system is generating about 200 – 250 mg/l of alkalinity, which is about all that can be expected. Now, concerns are being directed to the second vertical flow pond, which has steadily lost the ability to generate the additional alkalinity needed to fully neutralize the raw water. Both vertical flow systems are scheduled to be drawn down in the summer of 2002 to evaluate the development of preferential flow paths and take remedial action. One possibility is that the very aggressive flush system has actually pulled compost down into the limestone, causing the compost layer to be too thin above the pipes and allowing the development of preferential flow paths. The aggressiveness of the flush system is due to the large head differential between the system and the flush discharge point and the separation of the flushing system into 3 cells, allowing greater velocities when each is flushed individually. There is no evidence of metals plugging in either vertical flow wetland and the system continues to remove over 90% of the iron, 70 to 80% of acidity and about 60% of the aluminum (see Figure 1).

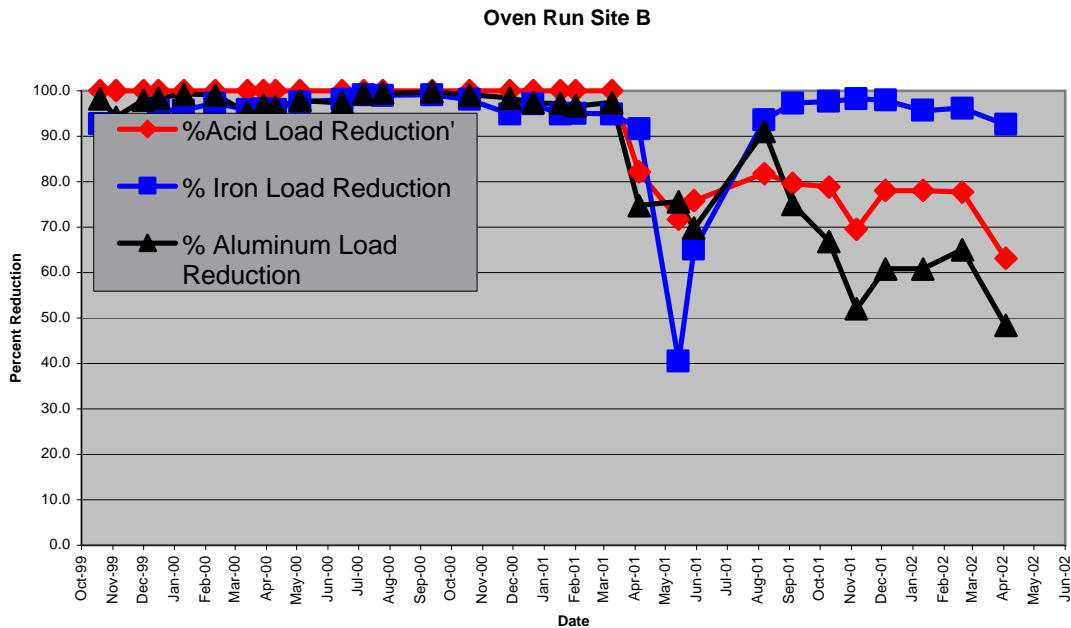


Figure 1

Oven Run Site C was completed in 1997 and consisted of backfilling a 5,000 foot long highwall using OSM Title IV funds. A small, but highly acidic, discharge from the open pit was largely eliminated. A minor seep that remains is directed to the Oven Run Site B system. Since backfilling this highwall, which was hydrologically connected to the deep mine discharge at Site B, maximum flows at Site B have been no more than half the flow measured prior to completion of this project. This flow reduction is a very important secondary benefit to completion of the backfilling project.

Oven Run Site D was completed in September of 1995 by NRCS, using PL-566 and section 319 funds. Site D treats approximately 100 gpm of moderately acidic deep mine drainage. Since beginning operation as the first completed system on Oven Run, the system worked well. In sequential order the system is composed of an initial settling pond, aerobic wetland, vertical flow wetland, settling pond, aerobic wetland, vertical flow wetland and a final settling pond. A rise in the water level in the first vertical flow wetland was noticed after the second winter of operation.

A limited flushing system in this system allowed for some flushing of accumulated metals from the system. Initially, the limited flush lowered the water level back to original levels. In subsequent years, the water level raised every winter when flow rates increased. Each time the system was flushed, the effectiveness of the flush decreased. A layer of iron was accumulating on top of the compost in the vertical flow ponds that limited the flow through the system. The system continued to treat the water flowing through it, but the quantity of water flowing through the system was controlled by the permeability of the iron on top of the compost. In the winter of 1999, some of the water began to flow through the emergency spillway and was not treated in the vertical flow wetland. This condition continued through the spring of 2002. At this point in time, approximately 50 GPM would pass through the system; any flow above this amount would bypass the system through the emergency spillways.

To remedy this situation, the Somerset County Conservation District applied for and received a DEP Growing Greener grant in the spring of 2002. To limit the iron accumulation on the compost, 3 rock filter dams were placed in the wetlands preceding the vertical flow ponds. The rock filter dams will eliminate short-circuiting of flow through the wetland and will increase the detention time in the wetland. An aggressive bottom flushing system was also installed to eliminate inert materials left behind by limestone dissolution and to remove metal accumulation in the rock layer. As part of the bottom flushing system, piping was extended to the surface of the compost and capped with threaded pipe caps. These vertical pipes will act as ports to flush accumulated iron from the surface of the compost. The caps will remain on the vertical pipes during normal operations of the system and be removed prior to flushing for surface iron removal.

Oven Run Site E was completed in 1997 with NRCS funds, and treats two moderately acidic deep mine discharges with a configuration very similar to Site B (two vertical flow wetlands and two settling ponds). Plugging of the vertical flow wetlands started to occur relatively soon after commencement of operation, which was very puzzling to the system designers. The problem was eventually determined to be the result of the limestone used in the vertical flow wetlands. While technical specifications called for a required calcium carbonate percentage, they did not specify rock meeting soundness standards as specified by the PA Department of Transportation (PA DOT, 2000). Initially, the rock produced good water quality, but the rock quickly began to deteriorate. After 4 years, hydraulic conductivity through the system was lost to the point that the system is not providing treatment. Designs have been prepared to replace the degraded rock and install an aggressive flushing system. Late summer of 2002 construction is planned for the upgrading of this system.

Oven Run Site F was completed in September of 2000 with NRCS funds. The design of this system was completed with much more knowledge about the operation and maintenance concerns of vertical flow wetlands. Experience at site D taught us that routine flushing from the bottom of the vertical flow wetland was necessary to keep the systems functioning over time. This system treats 300 GPM of acid mine drainage and consists of a vertical flow wetland, settling pond, vertical flow wetland and a final settling pond. A very intensive flushing system was designed for the vertical flow wetlands at this site. The vertical flow wetlands have a grid of 6 inch, perforated pipes on 11 foot centers, under the limestone. These pipes outlet to two, 12 inch pipes that are at opposite ends of the vertical flow wetland. The flow out of the system when these two pipes flow is approximately 5000 GPM per pipe, at the beginning of the flush. Experimenting with the sequencing of opening valves and the duration of flushes has provided some empirical observations of the flushing events at this site.

Observations were made while opening only one valve at a time, with alternate opening and closing, after 30 minutes of flow, and opening both valves at the same time until the vertical flow wetland was drained. With both flushing scenarios, the flush water was initially very turbid. With the alternate opening and closing of valves, the effluent water began to clear and become less turbid after 30 minutes of flushing. The amount of turbidity decreased with each successive alternate opening and closing of valves. When both valves were opened simultaneously and the water was allowed to flow until the system was drained, the effluent water remained very turbid during the entire time of the flush, approximately 3 hours. Since this system was constructed with an aggressive flushing system in 2000, quarterly flushing has been completed. There has been no indication of rising water levels in this system as were noted at Site D, where only a limited flushing system was designed. These empirical observations need

to be followed by more controlled flushing experiments that involve water quality testing during the flush to calculate quantities of metals flushed from the system.

CONCLUSIONS

The future of passive treatment of AMD is dependent upon resolution of the long term O, M & R issues related to these systems. Implementation of the DEP Workgroup recommendations is underway and starts to resolve these issues, particularly from an administrative standpoint. However, resolution of many of the technical concerns may be more difficult. One of PA's leading AMD treatment consultants, Hedin Environmental, received a Growing Greener grant to evaluate design and operation of flushing facilities. This work was initiated with a workshop attended by a number of government and consulting personnel to gather and organize existing data on vertical flow systems in order to design the most efficient systems (Workshop Proceedings, 2002). The technical issues fall under several general categories that are discussed below.

Use of Mushroom Compost:

The use of mushroom compost in vertical flow wetlands to promote biological activity and facilitate the conversion of ferric iron to ferrous iron is a widely accepted practice (although, more recent thinking is that this conversion is not a complete one; ferric iron is observed being flushed from these systems). Mushroom compost is also used in anaerobic wetlands to encourage sulfate reduction reactions and in aerobic wetlands to promote plant growth. When AMD systems are constructed using mushroom compost, sample analyses have shown a significant biological oxygen demand (BOD) present during the first week to 3 months the system is in operation. This BOD can present devastating impacts on receiving streams if any aquatic life is present. Frequently, the acid water being treated has already devastated aquatic life to the level that there is little need for concern. However, in situations where aquatic life is present or where there are downstream municipal water supplies, the management of the outflow of BOD from the system is imperative. The simplest method to control the initial flow of BOD is to strategically place piping and valves in the system so that the majority of the AMD can be bypassed around the system while a small flow is allowed to move through the system. The small flow will, with time, reduce the BOD to levels that are not harmful to aquatic life. Once this condition is reached, the flow of AMD through the system can gradually be increased until all of the AMD is flowing through the system. Recent trends have been toward a reduction in compost from early designs, where compost thickness was as high as two feet. Experience on the NRCS Oven Run sites indicates that 6 inches of compost is adequate to promote biological activity and facilitate conversion of ferric iron to ferrous iron. Larger quantities of compost take longer to dissipate the BOD and long-term odor problems can be a concern in residential areas. Another consideration, however, is that too little compost may contribute to short-circuiting, as well as possible rapid depletion of fine limestone within the compost and a possible loss of biological activity once the pH drops. BAMR has recently dropped compost specifications from 2 feet to 1 foot to reduce BOD generation while still providing adequate compost to address the other concerns.

Short Circuiting:

In Oven Run, we have learned that the flow through systems with under draining flush capabilities may short circuit in a number of ways. Preferential flow patterns may develop as a result of shifting compost below inflow points and possibly even above flush pipes on systems with aggressive flushing. Other short circuiting may occur directly through the flushing pipes. In long, narrow systems, with flush piping extending the full length of the system, there is a high potential for water to enter the flush pipes at the inflow end of the system and travel through the pipe instead of through the rock. This short-circuiting does not allow adequate detention time in the limestone rock for treatment of AMD. Short-circuiting can be reduced using a couple different methods. Distribution manifolds that evenly distribute the water throughout the vertical flow wetland prevent water from entering at one point and entering the flush system. This also keeps compost from being shifted immediately below the inflow point. Another method of preventing short-circuiting is to incrementally cap the longitudinal flush pipes so water is forced to leave the flush pipes and flow through the limestone rock (compartmentalizing the flush systems). On larger flow discharges, the use of both of these techniques is recommended to maximize water to rock contact. Minimizing the length to width ratio also should be considered during design.

Flushing:

Experience in Oven Run and other watersheds over the last seven years has clearly shown that vertical flow wetlands treating highly mineralized AMD that are not designed and operated with an aggressive flushing system will experience plugging with time. In vertical flow wetlands that treat acid mine drainage with dissolved iron and aluminum, the accumulation of precipitated metals in the rock will fill the rock voids, eventually plugging the system, and cease to treat the mine drainage. Bottom flushing of vertical flow wetlands has proven to be an effective way of removing accumulated precipitates from these systems. Long duration, high volume flushing performed on a regular schedule has maintained hydraulic conductivity through the Oven Run Site F system. The system has continued to produce high quality water since construction. Figure 2 illustrates how the water quality improves as it moves through the system.

Some system designers have recommended limiting the number of holes in the perforated pipe to increase the velocity of flow through each perforation in the pipe. The number of perforations in the pipe is the limiting factor determining the quantity of water leaving the system. There are some concerns with this type of design. One concern is that the distance between holes in the pipe becomes too great and the area of influence of the perforation is less than the distance between perforations. In this case, there potentially could be "dead areas" between perforations where little flow occurs, which would eventually cause the rock to plug with metal precipitate. Another concern is that limestone rock placed directly on the perforated pipe could greatly reduce the capacity of the perforations if a rock lodges in a perforation. If this happens, the distance between perforations becomes even greater, increasing the potential for "dead" areas. Other designs currently being evaluated include those using multi-tiered flush piping and those that do not use compost at all. Determining the best design for these systems is an ongoing process. Hedin Environmental has retained an engineer to evaluate current system designs and make recommendations for future designs. A draft paper, currently being circulated for comment, recommends increasing flush velocities to assist in the removal of retained solids by dividing the under drain systems into multiple cells and designing the header pipes for gravity flow to provide for even flow distribution (Langese, 2002).

Rock Quality:

The quality of the limestone rock used in vertical flow wetlands is somewhat dictated by the local commercially available sources of limestone. In western Pennsylvania, there are several sources of limestone that perform well over long periods of time. It is important to specify stone that is durable and will not deteriorate when exposed to acid. Specifying rock that meets the soundness standards specified by the Pennsylvania Department of Transportation (PA DOT) should ensure the integrity of the system with regard to ability to transmit water. Early in the implementation of the Oven Run Site E project, the soundness of the limestone was not specified by NRCS. Rock was provided that met the specified chemical standards, but was not from an approved PADOT quarry. This is believed to have caused the system to fail.

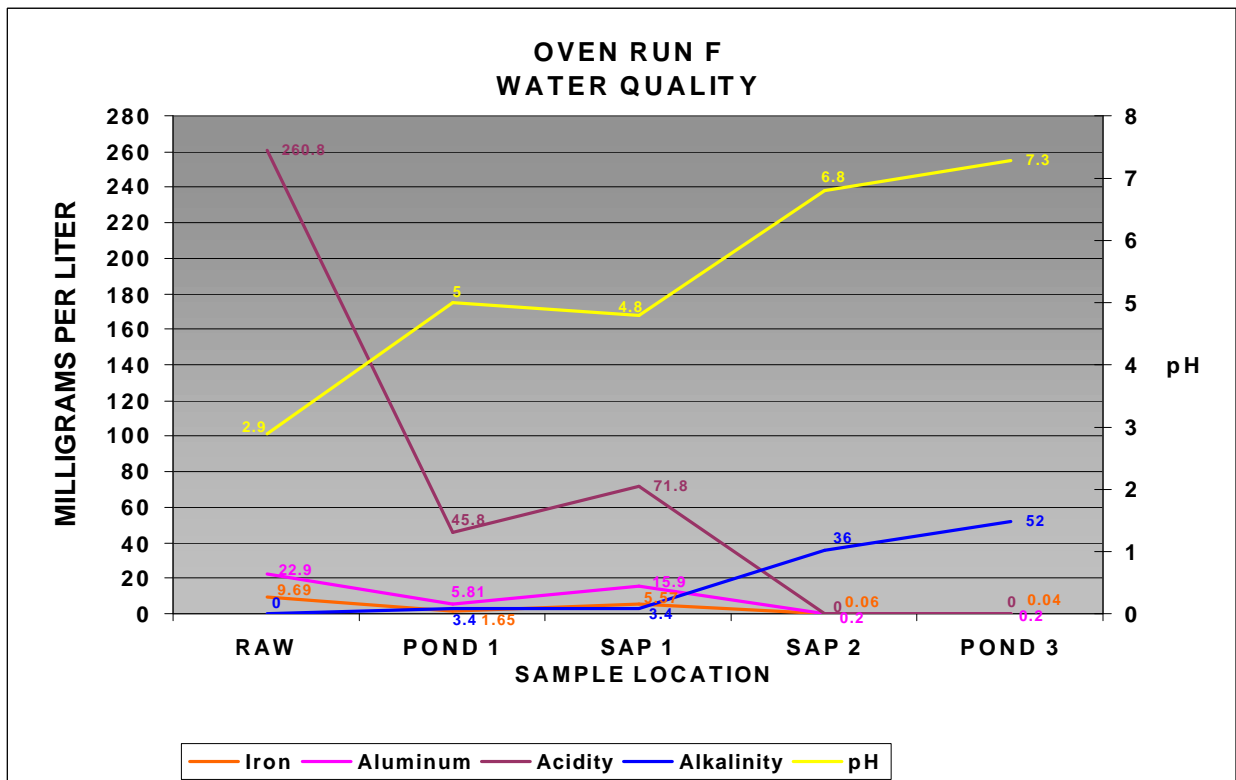


Figure 2

It is also important to specify a minimum of 80% calcium carbonate as determined by ASTM C-114. It is important to note that calcium carbonate equivalent (CCE) is not specified but elemental calcium carbonate is. Also, the maximum content of elemental magnesium should not exceed 2% and inert material (e.g. silica) should be less than 15%.

The above discussions should help to emphasize the need to have a knowledgeable, reliable entity to provide for long-term O, M & R. The failure to do so will result in the eventual failure to adequately treat AMD and the loss of millions of dollars worth of public investment. Gains in the restoration of aquatic habitat will also be lost. The design of these systems is expected to continue to evolve as more is learned about long-term operation. Passive treatment

of AMD is expected to be an important aspect of watershed restoration into the foreseeable future. O, M & R improvements will ensure the continued success of this restoration work.

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Attachment A

DEPARTMENT OF ENVIRONMENTAL PROTECTION

FINAL RECOMMENDATIONS OF THE LONG TERM OPERATION, MAINTENANCE AND REPLACEMENT WORKGROUP

November 15, 2001

An increasing number of watershed groups, as well as many Federal, State and local agencies, have become active in watershed restoration over the past several years. As a result, a large number of restoration projects are being funded and constructed. Water quality and aquatic habitat improvements are occurring as these projects are implemented. The need for long-term operation, maintenance and replacement (O, M & R) has been increasingly recognized as a requirement to ensure the success of watershed restoration projects. In Pennsylvania, a total of nearly \$93 million of public money has been spent on these projects since 1988 (see attachment A). The establishment of the Growing Greener grant program has greatly accelerated this effort. The failure to maintain the systems being constructed under these projects could have detrimental impacts to watersheds that are beginning to support an increasing number of stream uses. As a result of growing concern over this issue, the Department's Greener Team established a workgroup to provide recommendations to address this need. This workgroup consists of individuals from Federal, State and local governments, as well as private consultants and watershed group officials. All have had extensive experience in the operation and maintenance of watershed restoration projects.

It is important to note that, for the purpose of defining needs and determining costs, the workgroup defined long-term O, M & R as system operation and maintenance, plus one system replacement at the end of the design life of the project. Also of note is a decision by the group to include all publicly funded watershed restoration projects constructed through 2001, when determining costs associated with existing systems.

O, M & R Plan

An O, M & R Plan, developed by the project sponsor, is an integral part of providing for operation and maintenance of watershed restoration projects. The basic elements of an O, M & R plan include: a written agreement with the entities responsible for O, M & R, identification of tasks to be completed, development of a schedule and determination of responsible parties and costs. Plans must become a "deliverable" of all new implementation grants. For existing projects that have no O M & R plan, site-specific plans will need to be developed prior to receiving funds to address O, M & R.

Operation, maintenance and replacement concerns should begin at the initial site inventory of a project and continue through all phases of project development. Water quality information, along with flow measurements, should be looked at critically with respect to future operation and maintenance. If a site requires intense operation and maintenance to function, the sponsors of

the project need to understand the intensity and potential cost. Once the decision is made to move ahead with project design, the focus should be to make the operation and maintenance of the system as easy as possible. Prior to project implementation, the sponsors need to understand what it is they need to do and at what frequency. Additional training may need to be provided to facilitate a more detailed understanding of operation and maintenance.

In developing an O, M & R plan, the following should be considered:

Operations - Sponsors need to demonstrate an understanding of, and the ability to perform, routine duties, such as:

- Inspections (including water sampling and flow measurements);
- Litter control;
- Vegetation control;
- Mechanical maintenance (including flushing);
- Insect and vector control;
- Physical stability and erosion control.

Maintenance - Sponsors need to demonstrate an understanding of, and the ability to perform, more intensive items that may take considerable dollars and time to accomplish, such as:

- Removal and disposal of accumulated precipitate or sediment;
- Maintenance of channels;
- Industrial cleaning of pipes;
- Repairing damage after major storm events;
- Repairing cracks or leaks;
- Adding limestone, compost, sand or gravel;
- Repairing vandalism damage;
- Adjusting grade or outlet structures.

Replacement - Systems have a designed life expectancy; once that design life is exceeded, much of the system will need to be recharged or replaced. Replacement will involve much of the same effort originally needed to construct the system. Changes in technology and water quality and quantity will need to be considered to determine if the size and/or design of the system must be changed. Replacement considerations include:

- Estimating BMP (Best Management Practice) design life;
- Determining replacement responsibility, including a successor, in the event of the original project sponsor's inability to carry out these responsibilities;
- Determining approximate costs for the following possible needs: removing accumulated sediments, replacing defective valves, water control structures, re-sizing the system to accommodate changed water quality or quantity, recharging organic matter layer on wetlands, recharging limestone rock.

An O, M & R Plan should include:

- Narrative describing O, M & R needs and identifying responsible parties
- Signed maintenance agreement with all parties, including property owners
- O, M & R Site Map that includes BMP's, flushing points, monitoring points (water sample locations, benchmark cross sections, etc.)
- Site specific instructions
- "As-built" plans

Long-term Cost Analysis

Long-term costs are analyzed in many business and government applications. The starting point for most analyses is a spreadsheet that projects costs over the lifetime of the BMP. Costs are often divided into tasks such as site inspections, sample collection, sample analysis, sludge management, flushing, and reconstruction. A long-term cost spreadsheet should be developed for all projects early in the planning process. The construction of this spreadsheet will help sponsors to recognize long-term responsibilities and also encourage them to identify mechanisms that will legitimately lessen the long-term costs of their projects.

The workgroup collected information on long-term costs of BMPs by reviewing existing policies, interviewing technology experts, and by analyzing current cost data. The workgroup did not find established O, M & R cost estimates for mine drainage treatment systems, so estimates were developed from Department, Natural Resources Conservation Service (NRCS), non-profit and consultant experiences. These data were used to develop spreadsheets that projected long-term O, M & R costs for specific mine drainage BMPs. Development of the spreadsheets required assumptions about the time period over which to project costs and whether to include a BMP replacement in the extrapolation. The workgroup decided to analyze 25 years of costs and to include one replacement in the calculation.

The spreadsheets were analyzed in two ways. The first method was to calculate the present value of the long-term costs. The method requires financial assumptions about rates of inflation and investment return. The result of this calculation is a sum of money that, if the financial assumptions are realized, will yield proceeds adequate to cover all anticipated long-term costs. Our analyses assumed a 3% inflation rate and a 6% rate of return, or a net rate of return of 3%. While this may seem conservative, it is consistent with long-term economic trends in the U.S. It is also consistent with similar analyses of long-term AMD treatment costs being conducted by the Department for permitted mines. The present value analysis yields a sum of money that can be placed into perspective by comparing it to the BMP's original construction cost. On average, the present value of the long-term O, M, & R costs were approximately 60% of the construction costs. Thus, if the Department wanted to fully fund a \$100,000 passive treatment project, it should plan on placing \$60,000 in an interest-bearing account at the time of construction. If the cost projections and financial assumptions are correct, no more funds should be required for 25 years.

A second analytical method calculated the annual costs of an on-going O, M & R program. Instead of paying all the anticipated long-term costs in the first year, only those expenses anticipated for the current year would be paid. Each year, for 25 years (the workgroup's

analytical timeframe), the annual O, M & R costs would be paid. We calculated the average annual cost by summing all anticipated O, M & R costs and dividing by the analytical period (25 years). This average O, M & R cost was related to the construction cost to calculate the O, M & R factor. On average, most AMD passive treatment technologies had an average annual O, M & R factor of 4%. Thus, a \$100,000 project would require an average of \$4000 per year in annual costs. The actual costs would vary widely because major maintenance costs and replacement costs – both high expense items – occur infrequently and generally toward the end of the BMP lifetime. The factor does not account for inflation. Since most watershed restoration projects have been constructed relatively recently, not accounting for inflation shouldn't be a problem at this time. If the Department decides to fund O, M & R using the O, M & R factor, it should regularly adjust the base value of construction to account for inflation in the future.

The estimated O, M & R factors varied with the type of watershed restoration project. Table 1 shows the range in factors. Most of the BMPs being implemented with Growing Greener funds are in the 3-5% range. While the AMD factors were based on actual experiences of several workgroup members, the non-AMD estimates were derived from informal surveys of the following sources: NRCS, the Center for Watershed Protection, the Keystone Stream Team, PA DEP, MD DOE, Universities and consultants. These sources were able to provide good input concerning O & M (particularly the NRCS, which just completed an evaluation of agricultural BMP's by June C. Grabemeyer, Agriculture Economist, East Lansing, MI), but were less certain about replacement costs. The group decided that 4% was a good average O, M & R factor to use in estimating long-term costs for all types of restoration projects, for the purpose of estimating funding needs.

Table 1: Average O, M & R Factor for Watershed Restoration BMP's

Agricultural BMPs	
4%	
Stream Restoration BMPs	4%
Stormwater Management BMPs	3%
AMD Vertical Flow Systems	5%
AMD Anoxic Limestone Drain Systems	4%
AMD Compost Anaerobic wetlands	4%
AMD Pyrolusite© Systems	3%
AMD Open Limestone Channels	1%

The workgroup broke down the long-term O, M & R factor into cost categories. For a passive treatment system that has a 5% annual factor, system reconstruction accounted for 40% of the costs, routine operations (inspections, sampling, flushing) accounted for 20%, water sample analyses accounted for 10%, and general and unscheduled maintenance and repairs accounted for 30%. This breakdown was valuable because it showed that well-organized project sponsors should be able to cover up to 60 % of the estimated O, M & R costs by assuming all or part of the non-replacement responsibilities.

The workgroup decided to use the O, M & R factor method to analyze costs and make recommendations concerning the amount of funds needed to address O, M & R on a long-term

basis. This determination was made based on feedback received from Executive Staff and others that up-front, lump sum funding of O, M & R was not likely to be pursued by the Department.

A difficult issue within the analysis of long-term costs was the cost of lab analyses of water monitoring samples collected. The water sampling cost analysis was based on the Department's cost of \$65 per sample (approximate cost of the Bureau of Abandoned Mine Reclamation's 711 Standard Analysis Code, used for routine AMD samples). Private laboratories experienced with AMD analysis can provide reliable analyses for \$15-35 per sample, although inexperienced private labs sometimes provide inconsistent results. Two possible options were discussed with regard to sample analyses. One is for the Department to consider certifying private laboratories for AMD analysis and encourage watershed groups to use private labs, thereby decreasing long-term costs. Another option is for the Department to develop a regular funding source for analyses of watershed samples currently being collected under Mineral Resource Management's collector numbers. Costs can be reduced by determining a Standard Analysis Code that provides the minimum number of parameters needed to evaluate system performance. The advantages of this option are that lab results would be made available more easily to the Department and the quality assurance issues are addressed. However, it may be possible to address the quality assurance issue with private labs through a certification process. The workgroup has decided to recommend both options so that watershed groups can utilize what works best on an individual basis. The workgroup believes that the Bureau of Mining and Reclamation's existing SOAP/ROAP certification process is the best vehicle to use to certify private labs.

Implementation (Funding Engine)

Various funding options were reviewed by the workgroup to provide for the sustainability of existing and future facilities that benefit the general public and improve the water resources of the Commonwealth.

True sustainability needs local community ownership and involvement. Public-private partnering develops healthy interdependence (working relationship) between state agencies and the watershed residents, including volunteers, students, service groups, private industry, environmental professionals, and other interested parties.

Some project sponsors have developed and are implementing long-term plans; however, many groups currently do not have the means or ability to do this.

The workgroup developed recommendations for a support strategy to enable groups to provide for long term O, M & R. It includes the following:

- Commonwealth: develop a source of funding and create a grant funding category for the O, M & R of existing and future construction projects;
- Sponsor: provide available resources for total or partial O, M & R;
- Other: provide additional O, M & R support by use of the Bureau of Abandoned Mine Reclamation (BAMR) construction/maintenance crews, the 12th Congressional District Equipment Center, and local/private industry.

Funding Options:

The workgroup calculated the approximate initial annual funding needed to address long-term O, M & R at \$1.86 million, using the following method. This amount, discussed in both options below, has been calculated by determining the cost of providing for 50% of the average 4% O, M & R factor of \$93 million for existing projects. This amount is expected to cover major maintenance (10%, or approximately 1/3 of the expected total maintenance costs) and replacement (40%) needs. It is expected that watershed groups and their local partners, Department assistance with lab costs and BAMR and 12th Congressional District Equipment Center assistance with maintenance will make up the remaining 50% of the O, M & R factor.

The following are two alternatives developed by the workgroup as possible solutions to the funding challenges associated with long-term O, M & R. One of these alternatives, or a combination thereof, may ultimately be seen as the appropriate funding solution.

Option 1: Funding O, M & R on an annual-basis (“pay as you go”)

- Up to 10% of Growing Greener funds are earmarked for funding of O, M & R projects; the amount not spent for O, M & R is released to provide additional new project funding.
- The Secretary's approval is needed if demand is such that more than 10% of Growing Greener funds are necessary.
- Some of the 10% is held back for emergency O, M & R projects, with this money released for new project funding at the end of the fiscal year.
- The delivery system would be the existing Growing Greener Grant Center, using an additional funding category on the grant application form.

Advantages:

With this option, if the O, M & R amount is not fully requested, then the balance would be available for funding new projects. At the current Growing Greener funding level of \$50 million per year, it is expected that less than 10% of this amount will cover all major maintenance and replacement needs for the foreseeable future (expected to be about \$1.86 million for existing projects).

Disadvantages:

This option requires the continuation of Growing Greener beyond year five. At this time, continuation is considered likely, but is not a certainty. Also, if Growing Greener is continued, the funding level may be reduced, thereby reducing the amount available for O, M & R. Another disadvantage is that it will take away from money to be spent on new projects, unless the Legislature authorizes increased Growing Greener funding to make up the difference.

Option 2: Funding O, M & R for the long-term (“set aside”)

- The PA legislature provides an annual budget appropriation for long-term needs (or, an existing funding source is found within the Department) at an initial rate of \$1.86 million per year.
- The amount appropriated will need to increase annually based upon the amount spent on

construction projects annually. For example, if \$25 million worth of projects is constructed in 2002, there will be \$93 million plus \$25 million, or \$118 million worth of constructed projects; therefore, \$2.36 million will need to be appropriated for O, M & R the following year (50% of 4% factor multiplied by \$118 million).

- The annual appropriation would be placed in a "set-aside" fund administered and managed by the Commonwealth. Applicants would apply for funds using the established Growing Greener framework. Any money left over at the end of the year would stay in the fund. The fund would be allowed to build up so that, when needs become greater (as systems need replaced or major floods or other catastrophes occur), the funds would be available to cover that need.

Advantages:

This option would leave the current project funding amounts for Growing Greener intact and would not be dependent upon the continuation of Growing Greener beyond year five. It would allow an accumulation of funds to deal with long-term needs that are expected to increase as systems age and need to be replaced.

Disadvantages:

This option would require legislative action to appropriate funds. It would require the establishment and administration of an interest-bearing fund. It would require tracking of implementation projects from all public funding sources in order to know how much new construction takes place on an annual basis, to determine funding amounts.

Actions Needed by the Department for Implementation

- Select a funding option and appropriate funds for O, M & R support of existing and future projects.
- Develop a fund/program management system, including a Growing Greener O, M & R project category and related activities (including changes to scoring and application guidance).
- Require the development of O, M & R plans prior to the provision of O, M & R funds for existing projects and as a deliverable under construction contracts for new projects.
- Provide O, M & R training for watershed groups via Growing Greener workshops and watershed conferences, with assistance from others.
- Improve DEP capacity to assist groups with O, M & R:
 - Provide improved capacity of BAMR's construction crews to assist with major maintenance.
 - Dedicate funds to support Mineral Resource Management sponsored lab analysis for watershed groups and determine an appropriate Standard Analysis Code.
 - Adopt SOAP/ROAP lab criteria and cost guidelines for watershed sample analysis.

Appendix A

Publicly Funded Restoration Projects

	NRCS	319	BAMR	WRPA	OSM	G2	Totals
1988	\$125,000	\$0	\$0	\$0	\$0	\$0	\$125,000
1989	\$150,000	\$0	\$0	\$0	\$0	\$0	\$150,000
1990	\$0	\$75,000	\$0	\$0	\$0	\$0	\$75,000
1991	\$75,000	\$200,000	\$0	\$0	\$0	\$0	\$275,000
1992	\$12,000	\$225,000	\$0	\$0	\$0	\$0	\$237,000
1993	\$0	\$400,000	\$0	\$0	\$0	\$0	\$400,000
1994	\$0	\$675,000	\$0	\$0	\$0	\$0	\$675,000
1995	\$152,066	\$850,000	\$0	\$0	\$0	\$0	\$1,002,066
1996	\$0	\$1,000,000	\$0	\$0	\$0	\$0	\$1,000,000
1997	\$183,959	\$275,000	\$1,502,626	\$0	\$0	\$0	\$1,961,585
1998	\$34,314	\$1,700,000	\$1,664,737	\$0	\$0	\$0	\$3,399,051
1999	\$274,454	\$3,400,000	\$2,470,041	\$688,458	\$262,240	\$25,350,000	\$32,445,193
2000	\$109,284	\$2,700,000	\$643,873	\$296,558	\$567,800	\$21,050,000	\$25,367,515
2001	\$200,000	\$3,700,000	\$1,390,401	\$0	\$321,400	\$20,140,000	\$25,751,801
							\$92,864,211

Appendix C
Manganese Removal Papers

- a. Goodroad et al.
- b. M.A.T.S.

BIOREMEDIATION BY MIXED MICROBIAL MATS

M.A.T.S., Inc.
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Microbial mats. Microbial mats are natural heterotrophic and autotrophic communities dominated by cyanobacteria (blue-green algae). They are self-organized laminated structures annealed tightly together by slimy secretions from various microbial components. The surface slime of the mats effectively immobilizes the ecosystem to a variety of substrates, thereby stabilizing the most efficient internal microbial structure. Since mats are both nitrogen-fixing and photosynthetic (Paerl et al., 1989), they are self sufficient, solar-driven ecosystems with few growth requirements.

Microbial mats can be generated rapidly by enriching a water surface with ensiled grass clippings (silage). These constructed mats (CM) are durable, tolerant to a variety of toxins and resilient under changing environmental conditions. Additionally, the CM can easily be designed for specific remediation tasks by culturing desired microbes with the cyanobacteria/silage mixture. For example, mats with surface white rot fungus can be produced by this co-culture. Both components (algae and fungus) become tightly integrated and grow rapidly, as a leathery unit, over the surface of the water.

Removal of metals and metalloids by constructed mats. Mats, constructed with specific microbial components, have been developed for various bioremediation applications (Bender and Phillips, 1994). Mats have been found to reduce selenate to elemental selenium (Bender et al., 1991a), remove Pb, Cd, Cu, Zn, Co, Cr, Fe, U and Mn from water (Bender, 1992a; Bender 1991b; Bender et al., 1994a) and to remove Pb from sediments (Bender et al., 1989a). Uranium (0.1 mg/L of U²³⁸, spiked in groundwater samples) was removed in 3 h. Table 1 presents a summary of metal removal from water and sediments.

Organic degradation by constructed mats. Degradation of recalcitrant organic contaminants has been observed under both dark and light conditions (Bender and Phillips, 1994). The following contaminants have been degraded in water and/or soil media by constructed mats: TNT (Mondecar et al., 1994), chrysene, naphthalene, hexadecane, phenanthrene (Phillips et al., 1994), PCB (Bender, 1993), TCE (Phillips and Bender, 1993, unpublished) and the pesticides, chlordane (Bender et al., 1994b), carbofuran and paraquat (Murray, 1994, unpublished; Phillips and Bender, 1993, unpublished). Radio-labeled experiments with mat-treated carbofuran, petroleum distillates and TCE show that these three compounds are mineralized by mats and mat products, such as biofilms and biofloculents (Phillips and Bender, 1993, unpublished). Recently, in collaboration with the Institute of Paper Science and Technology, we have achieved a 50% reduction (eight-day laboratory treatment) in absorbable chlorinated organics in pulp and paper mill effluent waters. A summary of organic degradation is presented in Table 2.

Treatment of mixed contaminants. Recent data confirms that the mats effectively treat mixtures of organics and heavy metal. Mats simultaneously sequestered Zn and mineralized TCE and chrysene (Phillips and Rodriguez-Eaton, 1993, personal communication).

Immobilized mats. Mats produce slimy secretions which stabilize the members of the microbial community in their stratified structure and also adhere the entire community to a variety of substrates (clay, concrete, activated charcoal and glass wool). Several of these immobilized systems have been

effective in the bioremediation applications: (1) mat/glass wool in columns removed 6.3 g of Zn/Mn per M² per d (Bender et al., in press a) (2) mat/glass wool floaters removed 18.6 g Zn/Mn per M² per d (Vatcharapijarn, et al., 1994), (3) mat immobilized on clay mineralized carbofuran, chrysene and TCE (57% mineralization in 8 days with 48,000 dpm TCE applied directly to the mat, Phillips, 1993, personal communication).

Remediation mechanisms. Constructed mats offer a broad range of mechanisms related to the sequestration of heavy metals, the biodegradation of recalcitrant organics and remediation of mixed organic/inorganic contaminants such as TCE and carbofuran with heavy metals. The diverse microbial components within the mat define the range of molecular, cellular and communal mechanisms available in this ecosystem and likely account for the broad range of successful bioremediation applications demonstrated with this system. Diverse microbes organize into discrete microzones of highly contrasting oxic/anoxic character. These zones exist in close proximity and support aerobic/anaerobic communities simultaneously (Canfield and Des Marais, 1991), thereby offering a unique array of biochemical mechanisms for degradation of recalcitrant organics, such as chlorinated aromatics (Bender et al., 1994b).

Motile bacteria, associated with a mat growing on a soil surface, can penetrate clay soils and have been shown to degrade chlordane mixed within soil phase (Bender et al., 1994b; Murray, 1994, unpublished). Because heavy metal and metalloid contaminants are taken up and concentrated by mats in quiescent ponds (Vatcharapijarn et al., 1994; Bender et al., 1991a), the mechanism of metal transport through the water phase becomes an important question. Scanning electron microscopy/microanalysis research, correlated with chemotaxis studies of the motile bacteria suggest that these microbes become bonded to the metals, and migrate to the mat by responding chemotactically to the cyanobacteria and silage components. (Bender et al., 1989a,b).

Biofloculents likely play a key role in both metal sequestering and organic degradation. It has been found that the biofloculents, released by the mat, bind to heavy metals (Bender et al., in press b; Rodriguez et al., 1994) and also mineralize TCE and the pesticide, carbofuran (Phillips and Bender, 1993, unpublished). Additionally, the cell-free biofilm produced by the mats physically sequesters materials from the sediment region. An insoluble chlordane globule (7 mm dia; 2100 mg/L application level) was picked up by the biofilm, transported to the mat and degraded in 61 days (Bender et al., 1994b). Excised sections of the cell-free biofilm was recently demonstrated to mineralize TCE and carbofuran (Phillips and Bender, 1993, unpublished).

Mine Drainage Treatment.

Design. Acid coal mine drainage was delivered through a limestone, anoxic drain into an oxidation pond for removal of Fe. Three ponds (1 biological treatment pond, BTP, and 2 controls) 32-44 m², were constructed for final removal of Mn and residual Fe. These ponds, receiving drainage from the oxidation pond, were lined with PVC and layered with limestone rocks or pea gravel. A floating mat (1-2 cm thick), composed of filamentous green algae and cyanobacteria was developed in the BTP by enriching with ensiled grass clippings and microbial inocula (initially selected from the site). A second mat formed on the limestone at the pond bottom. Although mats were absent from control ponds, a thin layer (< 0.5 mm) formed over the rocks in these ponds.

Results. BTP removed 2.5 g/m²/d of Mn (Phillips et al., 1994). This removal rate was achieved within the first 2 m from the influent point and continued for approximately a year until the pond was drained. Although there was some Mn-cell binding, metals were primarily deposited as precipitates at the pond bottom. Unlike the control ponds, there was no evidence of metal release from the mat pond. Day/night and winter/summer metal removals were essentially the same. Fe entered the treatment pond primarily as a flocculated precipitate which became entrapped in the filamentous algae. Control ponds showed Mn breakthrough (Mn outflow releases > EPA regulations of 2 mg/L) during nighttime sampling or when mine drainage flow exceeded 4.5 L/min.

Mechanisms. Although the conditions of high oxygen and high Eh generated by the field pond mats may be central to the deposit of Mn oxides, other factors may be functional as well. Flocculents were

identified in the water column under the mat. Laboratory research showed that specific biofloculents were released by the mat in response to the presence of Mn^{+2} (Rodriguez-Eaton et al 1994). These materials carried surface charges ranging from -58.8 to -65.7 mV. The charges changed to +1.8 in the presence of divalent metal, indicating metal-binding to the biofloculent.

No soil was layered in the pond, so the predictable microbial ecology characterizing the sediment region may not be present in this system. The primary mechanisms of deposit likely were determined primarily by the chemical/biological processes mediated by the mat.

Patent. The Silage-Microbial Mat Construction and Method mentioned herein was the basis for a series of claims for patent protection before the US Patent and Trademark Office in March 1993. In January 1994, notification was received that all claims made by Bender and Phillips were accepted. A patent is being issued to Bender and Phillips.

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TABLE 1. Metal, metalloid and radionuclide removal in quiescent laboratory ponds.

Static laboratory ponds	Initial concentration, mg/L	Removal rate, mg metal/m ² mat/h
Free floating mats	Pb: 117	129
	Se: 37	6
	U ²³⁸ : 0.12	3.19
Mat immobilized on glass wool layered in baffled tanks	<u>Mix of</u>	
	Cr: 24	10,129
	Co: 24	10,052
Mat immobilized on floaters	<u>Mix of:</u>	
	Zn: 22	313
	Mn: 18	462
Excised mats	<u>Mix of:</u>	
	Cu: 284	378
	Zn: 3,021	3,778
	Cd: 19	356
Field pilot: acid mine drainage	Initial concentration, mg/L	Removal rate, mg metal/m ² mat/d
	Mn: 3.3 - 6.5	2.59

Free floating mat. Self-buoyant mats were cultured on the surface of laboratory ponds containing Pb or Se. Initial solution of selenate was reduced in part to elemental selenium which deposited in the surface mat (Bender et al. 1991a). Pb was deposited in the mat as PbS (Bender et al. 1989). The pH for the free floating mats was 6 to 8.

Mat immobilized on floaters. The mat was attached to glass wool balls that were floated in Zn/Mn-contaminated water at pH 7 to 9 (Bender, 1992b).

Excised mats. Small sections of mat were excised and applied to a mixed solution of Cu, Zn, Cd, and Fe sample from Iron Mountain Mine drainage in California (Bender et al. 1991b). The pH was adjusted to 3 to 4 before adding mat sections.

Microbial/green algae mat. A floating mat (1-2 cm thick), composed of filamentous green algae and cyanobacteria was developed by enriching with ensiled grass clippings and microbial inocula (initially selected from the site). A second mat formed on the limestone at the pond bottom.

TABLE 2. Biodegradation of contaminants by microbial mats.

Contaminant	Concentrations, mg/L		Time and % degradation	Mineralization
	Initial	Final		
2,4,6-trinitrotoluene (TNT)	100	<1	>99% in 6 days	
2,4-Dinitrotoluene (DNT)	217	26	88% in 4 days	NP
Chlordane in water	2,100	61	97% in 35 days	+
in soil	200	146	27% in 25 days	
Petroleum distillates ⁽¹⁾				
hexadecane	768	697	9% in 90 days	+
phenanthrene	374	284	24% in 90 days	+
chrysene	157	125	20% in 90 days	
PCB (3 Cl)	50	40	20% in 15 days	
(6 Cl)	100	63	37% in 33 days	
Pulp & paper mill Chlorinated organics	26	11	66% in 1 day	NP
Color reduction			39% in 1 day	
<u>Soil mix of:</u>				
Paraquat	50	29	42% in 21 days	NP
+ Carbofuran	50	20	60% in 21 days	+
<u>Mixed organic + inorganic:</u>				
TCE + Zn	Simultaneous mineralization of TCE			+
Chrysene + Zn	and chrysene with Zn sequester			+

Experimental. Mineralization experiments were performed with C¹⁴-labeled substrate; detection of entrapped labeled carbon dioxide determined percent mineralization. Occurrence of metabolic products in the water column and mat matrix confirmed that the process was degradation rather than simple adsorption. Soil/chlordane and pulp and paper mill experiments are in progress; no attempt has been made to identify metabolic products in these experiments. NP = mineralization experiments were not performed. In mixed contaminants no inhibition of processes was observed. The rates of organic degradation and metal sequestering were essentially the same in mixture as they were in single contaminant exposure.

Credibility of data results: Experiments were performed in three triplicate trials except in cases where radio-labeled materials prevented this number. In such cases single experiments were performed with triplicate trials (reaction flasks). In metal-sequestering experiments, mass balances fell within acceptable limits ($\pm 1\%$). Every sample set included a calibration of the instrument. In chlordane-degradation experiments, parallel analyses were performed by two commercial laboratories. Results verified that 10 mg chlordane applied below the mat was reduced to <1 mg in 5-7 days.

References: TNT = Mondecar et al., 1994; Chlordane = Bender et al., 1994; Petroleum distillates = Phillips et al., 1994; PCB = Bender, 1993; TCE, chrysene, carbofuran, paraquat = Phillips and Bender, 1993, Report to Pacific Northwest Laboratories Battelle.

POTENTIAL FOR BIOREMEDIATING USING CONSTRUCTED MIXED MICROBIAL MATS

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ABSTRACT

Microbial mats are natural heterotrophic and autotrophic communities dominated by cyanobacteria (blue-green algae). They are self-organized laminated structures annealed tightly together by slimy secretions from various microbial components. The surface slime of the mats effectively immobilizes the ecosystem to a variety of substrates, thereby stabilizing the most efficient internal microbial structure. Constructed microbial mats can be generated rapidly by enriching a water surface with ensiled grass clippings. These constructed mats are durable, tolerant to a variety of toxins and resilient under changing environmental conditions. The mats can be designed for specific tasks by inoculating the cyanobacteria/silage with selected microorganisms. Mats constructed with specific microbial components have been developed for various bioremediation applications: removal of metals, organic degradation, treatment of mixed contaminants, biological treatment ponds, and soil remediation. Constructed mats offer a broad range of mechanisms related to the sequestration of heavy metals, the biodegradation of recalcitrant organic compounds, and the remediation of mixed organic/inorganic contaminants such as TCE and

carbofuran with heavy metals. Diverse microbes organize into discrete microzones of highly contrasting oxic/anoxic character. These zones exist in close proximity and support aerobic/anaerobic communities simultaneously, thereby offering a unique array of biochemical mechanisms for degradation of recalcitrant organics such as chlorinated aromatic compounds. Because heavy metal and metalloids contaminants are taken up and concentrated by mats in quiescent ponds, the mechanism of metal transport through the water phase becomes an important question. Studies of the chemotaxis of the motile bacterial suggest that these microbes become bonded to the metals and migrate to the mat by responding chemotactically to the cyanobacteria and silage components. Biofloculants produced by the mats likely play a key role in both metal sequestering and organic degradation. It has been found that the biofloculants released by the mats bind to heavy metals. Additionally, the cell-free biofilm produced by the mats physically sequesters materials from the sediment region. Motile bacteria, associated with a mat growing on the surface of a clay soil, have been shown to degrade chlordane mixed within the soil phase. Biological treatment ponds using the constructed mats were developed

for treating acid coal mine drainage. The biological treatment ponds were operated for a year to remove Fe and Mn from the mine drainage. In laboratory studies, it was observed that specific bioflocculants were produced by the mats in response to the metals. The diverse microbial components within the mat define the range of molecular, cellular, and communal mechanisms available in this ecosystem and likely account for the broad range of successful bioremediation applications demonstrated with this system.

INTRODUCTION

Microbial mats

Microbial mats are natural heterotrophic and autotrophic communities dominated by cyanobacteria (blue-green algae). They are self-organized laminated structures annealed tightly together by slimy secretions from various microbial components. The surface slime of the mats effectively immobilizes the ecosystem to a variety of substrates, thereby stabilizing the most efficient internal microbial structure. Since mats are both nitrogen-fixing and photosynthetic (1), they are self-sufficient, solar-driven ecosystems with few growth requirements.

Microbial mats can be generated rapidly by enriching a water surface with ensiled grass clippings (silage). These constructed mats (CM) are durable, tolerant to a variety of toxins and resilient under changing environmental conditions. Additionally, the CM can easily be designed for specific remediation tasks by culturing desired microbes with the cyanobacteria/silage mixture. For example, mats with surface white rot fungus can be produced by this co-culture. Both components (algae and fungus) become tightly integrated and grow rapidly, as a leathery unit, over the surface of the water.

Patent

The microbial mat treated herein was the basis for a series of claims by Bender and Phillips for patent protection before the US Patent and Trademark Office in March 1993. In January 1994, notification was received that all claims made were accepted for the patent.

Removal of metals, metalloids, organic contaminants and mixed wastes by constructed constructed mats

Mats produce slimy secretions which stabilize the members of the microbial community in their stratified structure and also adhere the entire community to a variety of substrates (clay, concrete, activated charcoal and glass wool). Mats, constructed with specific microbial components, have been developed for various bioremediation applications (2). Degradation of recalcitrant organic contaminants has been observed under both dark and light conditions in water or soil (Table 1). Mats have been found to remove heavy metals from water and sediment (Tables 2 and 4). In collaboration with the

Institute of Paper Science and Technology, we have achieved a 50% reduction (eight-day laboratory treatment) in absorbed chlorinated organics in pulp and paper mill effluent waters. Recent data confirms that the mats effectively treat mixtures of organics and heavy metals (Table 3).

MATERIALS AND METHODS

Preparation of mats

Microbial mats are generated by enriching a water surface with ensiled grass clippings (7 g wet wt/L). Inocula of desired microbes are added with the silage. These microbes can be supplied as small sections of mature mats (maintained as desiccated or wet stock supply) or as separate strains of the constituent bacteria (cyanobacteria, purple autotrophic bacteria, and a variety of aerobic/anaerobic heterotrophs). The microbial consortium self-organizes in 5-7 days and forms a leathery sheet around the silage. Depending on the format of the remediation application, mats can be cut and added as excised sections, packed into columns, grown out on soil or sediment, floated on pond surfaces, layered in baffled tanks or broadcast over an inert substrate (i.e., organic mesh or glass wool). The mat grows and attaches to most substrates forming immobilized cell preparations.

Application of contaminants and conditions

Except for samples from the Iron Mountain Mine (IMM), initial pH levels in all experiments were 7-8; pH levels generally rose to 8-9 during the light period, and declined back to 7-8 during dark periods. The IMM samples were initially adjusted to pH 3-4 before adding the excised sections of mat. Metal precipitates, resulting from the pH elevation, were removed by settling before beginning the experiments. Initial concentrations listed in Table 1 represent those levels of soluble metals remaining after this initial metal removal. Except for the field pond experiments, the metal sequestering experiments were performed in continuous light. A 12/12 h light-dark cycle was used for organic degradations, unless otherwise indicated in the data table. Metals were added as soluble nitrates. Organics were generally solubilized in a solvent before adding to mats and water columns. In the case of contaminants which had very low solubility (TNT) or those added in concentrations that exceeded the solubility level (chlordane) the liquid globules or solid particles were allowed to remain at the bottom of the reaction flask. This posed no problem because contractile biofilms, generated by the mats, actively transported the materials to the surface where they became enmeshed in the mat matrix. In the case of chlordane/soil experiments, chlordane was mixed in clay soil. Mats were cultured on the moist soil surface. Experimental controls were either the contaminant placed under experimental conditions without mats or with heat-killed mats.

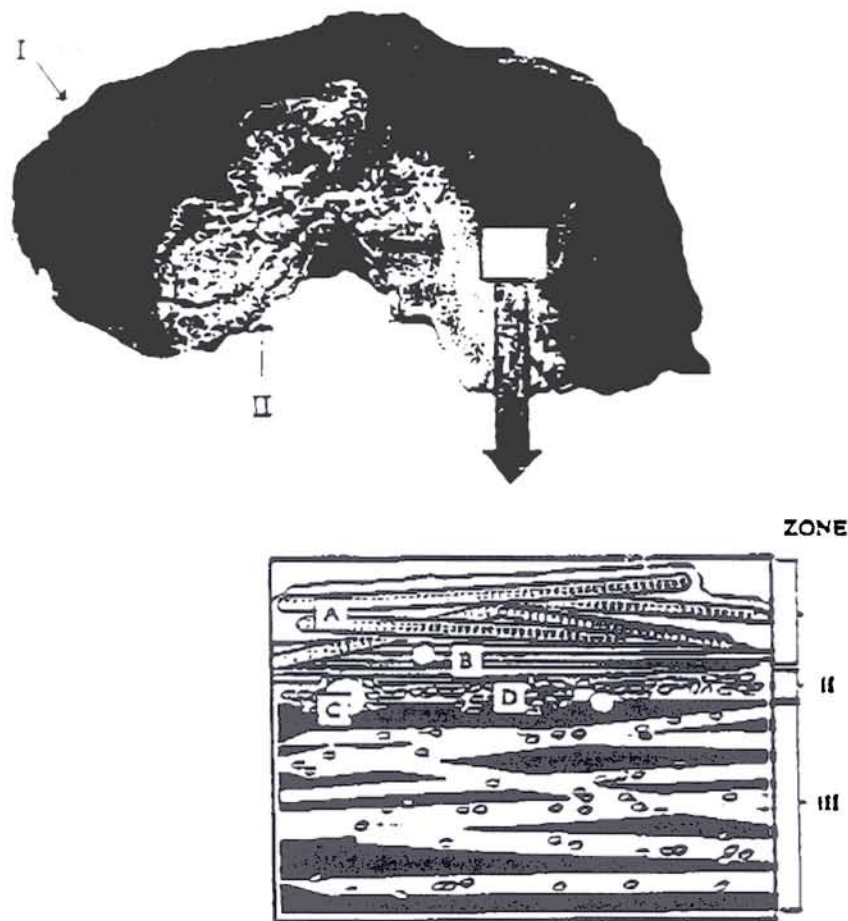


Fig. 1. Upper. Mat immobilized on glass wool floaters showed 70% (wgt/wgt) metal binding on mass and associated organic material. I = mat contains 43 mg metal/g organic Lower. Schematic of microbial mat attached to ensiled grass clippings. Zones: I = photosynthetic zone with cyanobacteria (A), II = heterotrophic bacteria (D) colonized around ensiled grass (B), III = glass wool with associated bacteria and organic residues released from the surface. Entrapped gases (C) maintain the buoyancy of the mat. Approximate depth for Zones 1, 2 and 3, respectively are 2 mm, 1 mm and 3.5 cm.

In Table 2 the Cr/Co removals show the highest rates using a baffled tank/immobilized mat system. Although the metal removal levels were reduced to <50% by the last 5 flows, the mats remained live and, after an addition of minimal salts medium, continued to grow. The uranium removal data in Table 2 shows that mats not only deal with high levels of inorganic contaminants, but can detect and remove μg concentrations as well.

Metal analysis of the mat and associated organics from the floating mat experiments show a 70% wt/wt binding of the metals to the mat material. This results in a discrete unit of mat-metal enmeshed in the glass wool floater (Fig. 1). The product might be subsequently vitrified into a concentrated pellet for metal disposal.

Field treatment of mine drainage

Acid coal mine drainage in Alabama was delivered into 32-44 m^2 ponds for removal of Mn. A floating mat (1-2 cm thick), composed of filamentous green algae and microbial mat, was developed in one pond. A second mat formed on the limestone at the pond bottom. The pond with an algae mat removed 2.5 $\text{g}/\text{m}^2/\text{d}$ of Mn (9). This removal rate was achieved within the first 2 m from the influent point and continued for approximately a year until the pond was drained. Although there was some Mn-cell binding, metals were primarily deposited as precipitates at the pond bottom. Unlike the control ponds, there was no evidence of metal release from the mat pond. Metal removal was essentially the same during day/night and winter/summer conditions. Control ponds showed Mn breakthrough (Mn outflow releases > EPA

Design of contaminant/mat exposure

Organic materials were generally added to the water column under the mat in a quiescent system. Only in the case of DNT was slow shaking (50 rpm) applied. Inorganic contaminants were applied in several design formats. Uranium was added to actual groundwater samples taken from the Department of Energy site at Hanford, WA. Chromium and cobalt (in mixed solution) were passed through a baffled tank layered with glass wool with an immobilized mat (each flow: 200 ml of 20 mg/L each metal, passed through baffle in 40 sec). In IMM experiments excised mats (9 cm²) were added to quiescent system containing 200 ml sample, diluted 1:1 with silage wash medium. Floating mats (floaters) were prepared with 4 g glass wool containing mats (1-2 mm) immobilized on the surface. These were applied to 1 L of mixed metal solution (18-22 mg/L Zn + Mn).

Field pond experiments

Microbial mat bound to green algae in a limestone-lined pond was used for manganese removal from coal mine drainage in Alabama from August 1992 to the present. Mine drainage flowed from a seep, through an anoxic drain and into an oxidation pond. Before entering the biological treatment pond, the oxidation pond water flowed through a trickling filter to remove some of the water's iron content. All microorganisms were isolated from the site, cultured in the laboratory and returned to the site for inoculation. Green algae initially established voluntarily. Control ponds included one with only a limestone substrate and another with a pea gravel substrate. Water quality parameters monitored were manganese and iron concentrations, temperature, dissolved oxygen, pH, redox, conductivity and alkalinity. Water flow rates averaged 4.2 L/min.

Sample preparation and analysis

Organic degradation experiments. All methods described below were taken from EPA SW-846 (8). Water columns under mat were extracted by separatory funnel liquid-liquid extraction method #3510. Solids (mats or soil) were extracted by either Soxhlet method #3540 or ultrasonic extraction method #3550A. Analysis of residual parent compound and metabolic products were performed as follows: PCB/chlordane: GC method #8080A with electron capture detector. Column was Supelcoport 100/120 mesh coated with 1-5% SP-2250/1-95% SP-2401 packed in a 1.8 m x 4 mm ID glass column or equivalent (Supelco, Inc.). Carrier gas of 5% methane/95% argon was used at a flow rate of 60 ml/min and 200° isothermal. TNT/DNT: HPLC method #8330 with UV detector, 254 nm. Column was reverse phase Supelcosil-LC-18, 25 cm x 4.6 mm x 5 µm packed with 5 µm spherical silica (Supelco, Inc.). Mobile phase was isocratic at 50% methanol/50% water with flow rate of 1.5 ml/min. Injection volume was 100 µL.

Metal sequestering experiments. All samples were digested prior to analysis by a CEM MDS-2000 microwave oven. Liquid samples were digested with trace metal grade nitric acid for a time period of 3 cycles of 10 mins each and a maximum permissible pressure of 80 psi. Solid samples were digested similarly for a 5-cycle period: first 3 cycles of 5 mins each and last 2 cycles of 10 mins each, with a maximum permissible pressure of 80 psi. Digested samples were analyzed for metal concentration with Varian Spectra-20 Atomic Absorption Spectrophotometer.

Organic mineralization experiments. Eight organic substrates were tested for the ability of microbial mat to mineralize them to ¹⁴CO₂ (Table 4). Experiments were conducted in a closed quiescent system with mat floating on water. In additional experiments, TCE, chrysene and carbofuran were applied to soil. Mineralization rates were determined by the amount of radioactivity (¹⁴CO₂) present in a potassium hydroxide trap. In the case of chlordane and hexachlorobiphenyl (PCB), a ¹⁴C budget determined the amount of ¹⁴CO₂ remaining in the water and re-incorporated into microbial mat via photosynthesis. Thin-layer chromatography was used to separate parent compound and dechlorinated metabolites. Visualization of spots by autoradiography and scintillation counting was used for parent compound and metabolites. TCA precipitation followed by 8-9 washes was the technique used to determine if ¹⁴C was in the protein fraction of the microbial mat.

RESULTS AND DISCUSSION

Explanation of experimental results

Bioremediation results are described in Tables 1, 2, 3 and 4. The microbial mats were effective in removing and/or degrading each class of compounds, including the mixture of TCE and Zn. Metabolic products were observed in all organic degradation experiments. In the case of DNT, eight metabolites were observed over a 25-day treatment. Metabolite identification is in process; 2-Methyl 5-Nitro Aniline has been confirmed. However, six of the eight metabolites disappear over time.

Mineralization experiments showed complete degradation with several recalcitrant compounds including hexachloro-PCB and chlordane. In a three-week treatment ¹⁴C-chlordane, mass balance analysis of the carbon label showed that 17% was recovered as CO₂, 78% as mat protein and 2% as highly polar metabolites (Bender et al., in preparation). No parent compound was recovered. This complete degradation occurred only in a dark/light cycle (12/12 h). When mat was exposed to chlordane under continuous darkness, significant quantities of parent compound were recovered. The chlordane/soil data is considered to be a preliminary result, until the experiments are confirmed with labeled chlordane.

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TABLE 1
REMEDIATION OF ORGANIC CONTAMINANTS BY MICROBIAL MATS

ORGANIC CONTAMINANT ^a	INITIAL CONCENTRATION mg/L or mg/kg	TIME AND % DEGRADATION ^b
2,4,6-trinitrotoluene	100	>99% in 6 days
2,4-Dinitrotoluene	217	88% in 4 days
Chlordane In water	2,100	97% in 35 days
In soil	200	27% in 25 days
Hexachlorobiphenyl (PCB)	100	37% in 33 days

Microbial mats were applied as free-floating mats on the surface of contaminated water (except with the soil/chlordane experiment in which mat was applied to soil surface and chlordane was mixed in soil). Where the organic substrate was insoluble in water, contractile biofilms generated by the mat actively sequestered the contaminant globule. (13) (14) (15)

b. Degradation was distinguished from simple absorption by disappearance of parent compound from the mat and water, occurrence of metabolic products and mineralization experiments (the latter is presented in Table 4).

TABLE 2
REMEDIATION OF INORGANIC CONTAMINANTS BY MICROBIAL MATS

INORGANIC CONTAMINANT	INITIAL CONCENTRATION, mg/L		REMOVAL RATE mg metal/m ² mat/h
Free floating mats ^a	U ²³⁸	0.12	3.19
Mat immobilized on glass wool and Layered in baffled tanks	Mix of		10,129 10,052
	Cr	24	
Mat immobilized on floaters ^b	Co	24	
	Zn	22	313
Excised mats applied to Iron Mountain mine sample ^c	Mn	18	462
	Cu	284	378
	Zn	3,021	3,778
Acid mine drainage ^d	Cd	19	356
	Mn	3.3 - 6.5	2.59 mg Mg/m ² /day

a. **Free floating mat.** Self-buoyant mats were cultured on the surface of laboratory ponds' surface mat. Pb was deposited in the mat as PbS. The pH for the free floating mats was 6 to 8. (17)

b. **Mat immobilized on floaters.** The mat was attached to glass wool balls that were floated in Zn/Mn-contaminated water at pH 7 to 9. (16)

c. **Excised mats.** Small sections of mat were excised and applied to a mixed solution of Cu, Zn, Cd, and Fe sample from Iron Mountain Mine drainage in California, a Superfund site. The pH was adjusted to 3 to 4 before adding mat sections. (5)

d. **Pond treatment of acid mine drainage.** A floating mat (1-2 cm thick), composed of filamentous green algae and cyanobacteria was developed by enriching with ensiled grass clippings and microbial inocula (initially selected from the site) on a 40 m² field pond. A second mat formed on the limestone at the pond bottom. (9)

TABLE 3 REMEDIATION OF MIXED WASTE BY MICROBIAL MATS

MIX WASTE CONTAMINANT	INITIAL CONCENTRATION, mg/L		REMOVAL/MINERALIZATION ^a	
Free floating mats	Mix of TCE + Zn			
	¹⁴ C-TCE	0.002	TCE	147 µg/kg mat. mineralized
	Zn	20	Zn	264 mg/m ² /h
	Mix of chrysene + Zn			
	¹⁴ C-chrysene	0.079	Chrysene	59 µg/kg mat. mineralized
	Zn	20	Zn	Not determined

a. Mineralization experiments were performed with C¹⁴-labeled TCE or chrysene; detection of entrapped labeled carbon dioxide determined percent mineralization. With mixed contaminants neither inhibition of organic contaminant mineralization nor metal sequester were observed. For example, TCE + Zn mineralized at a rate of 147 µg/kg, whereas TCE alone mineralized at a rate of 119 µg/kg. Chrysene + Zn mineralized at a rate of 59 µg/kg, whereas chrysene alone mineralized at a rate of 64 µg/kg. (18)

TABLE 4 MINERALIZATION OF ORGANIC CONTAMINANTS BY MICROBIAL MAT

ORGANIC CONTAMINANT ^a	INITIAL CONCENTRATION µg/L	TIME AND % DEGRADATION	LIGHT/DARK CONDITIONS
Petroleum distillates			
hexadecane	768	9% in 90 days	dark
phenanthrene	374	24% in 90 days	dark
chrysene	157	21% in 90 days	dark
TNT	<1000 ^b	4% in 45 days	dark
Chlordane	133	13% in 21 days	12L:12D
PCB	133	17% in 21 days	12L:12D
TCE	2	21% in 15 days	dark
Carbofuran	12	4% in 15 days	dark

a. Microbial mats were applied as free-floating mats on the surface of contaminated water. Mineralization experiments were performed with C¹⁴-labeled substrate; detection of entrapped labeled carbon dioxide determined percent mineralization. (18) (19)

b. Exact concentration not available.

regulations of 2 mg/L) during night-time sampling or when mine drainage flow exceeded 4.5 L/min. Although the conditions of high oxygen and high Eh generated by the field pond mats may be central to the deposit of Mn oxides, other factors may be functional as well and are described below.

Possible remediation mechanisms

Mixed microbial remediation systems have several distinct advantages. Specific detoxification mechanisms unique to all constituent strains of the mat are accessible in the consortium. Thus a broader variety of cellular releases (enzymes, bioflocclents) are available with the mat consortium than with a treatment system dominated by a single microbial strain.

The mat consortium generates micro-zones of unique chemistry characterized by discrete oxic and anoxic zones throughout the microbial matrix (Fig. 1). This phenomenon is amplified by the close association of phototrophs and heterotrophs. Thus, reductive dechlorination can likely occur by anaerobic processes in the anoxic zones, while carbon ring lysis is accomplished by the aerobes in the adjacent oxic zones. The rapid mineralization of chlordane might be explained by this community micro-structure of the mat. Either metabolic process (aerobic or anaerobic) can be amplified in mat by simply changing the light intensity and duration, thereby altering the conditions of Eh, pH and oxygen concentration.

Metal sequestering and interment of metals are likewise controlled both at the cellular/molecular and the community levels. Certain species of cyanobacteria produce negatively charged, flocculating macromolecules, which likely bind to the metals in the water column (10). This provides initial protection to the microbial community contacting the toxic metal. At the community level, the anaerobic zones harbor sulfur reducing bacteria (11), which generate hydrogen sulfide in the anoxic zones. Thus, sulfide is available for metal precipitation in the interstitial spaces of the mat. High concentrations of oxygen, produced during photosynthesis, becomes entrapped in the mat surface slime. Oxygen, therefore, remains available for oxide precipitation over long time periods in the photosynthetic zone of the mat.

The uptake of hexavalent chromium [Cr(VI)] at neutral to alkaline pH values of these studies suggests that the process is, at least to some extent, microbially mediated. This observation is based on several considerations. Hexavalent chromium is, in all of its forms, highly soluble in water and, consequently, unlikely to be precipitated or otherwise bound in high loadings by the microbial solids of the mats. The trivalent form of chromium which is the likely terminal oxidation state of

any reduction of the hexavalent chromium is an excellent cationic form for deposition as solid Cr(OH)₃, which has a pK of 37. However, conversion of hexavalent chromium to trivalent chromium will not occur at these elevated pH levels even in the presence of high concentrations of organic electron donors (12). In studies on the reduction of hexavalent chromium by *E. coli*, it was found that chromium reduction occurred concurrently with the respiration of organic electron donors such as glucose.

Based on these considerations, the rapid uptake of chromium to very high loadings in these mat studies suggests strongly that the process was mediated by some enzyme or other active reduction catalyst which is elaborated by the mat system as a defense mechanism. The mechanism acts to convert the highly toxic hexavalent chromium to the far less hazardous trivalent form which is precipitated rapidly as the hydroxide at the ambient neutral to alkaline pH levels.

The high uptake of cobalt by these mats systems was likely a consequence of simple precipitation as some sparingly soluble cobalt salt. Obvious candidates as precipitating anions are hydroxide, carbonate and, given the known presence of strongly reducing microzones in the mats, sulfide. At present, there is insufficient data to distinguish among these alternatives. Nonetheless, the mat systems appear to have very high capacities for uptake of cobalt.

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Appendix D
Solid-Reactant SRB Bioreactors

Papers by Jim Gusek et al.

THE CHALLENGES OF DESIGNING, PERMITTING AND BUILDING A 1,200 GPM PASSIVE BIOREACTOR FOR METAL MINE DRAINAGE WEST FORK MINE, MISSOURI¹

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Abstract. An active underground lead mine produces water having a pH of 8.0 with 0.4 to 0.6 mg/L of Pb and 0.18 mg/L of Zn. A full-scale 1,200 gpm capacity bioreactor system was designed and permitted based on a phased program of laboratory, bench and pilot scale bioreactor testing; it was constructed in mid-1996. The gravity flow system, covering a total surface area of about five acres (2 ha), is composed of a settling basin followed by two anaerobic bioreactors arranged in parallel which discharge into a rock filter polishing cell that is followed by a final aeration polishing pond. The primary lead removal mechanism is sulfate reduction/sulfide precipitation. The discharge has met stringent in-stream water quality requirements since its commissioning. The system was designed to last about 12 years, but estimates suggest a much longer life based on anticipated carbon consumption in the anaerobic cells.

Key words: Metal Mine Drainage, Lead, Zinc, Passive Treatment, Anaerobic Bioreactors

Introduction

Asarco's West Fork Unit is an underground lead-zinc mine that discharges water from mine drainage to the West Fork of the Black River (West Fork) under an existing NPDES permit. The adoption of water quality based discharge limits in its NPDES permit issued in October, 1991, prompted Asarco to evaluate treatment methods for metal removal.

Evaluations of alternative treatment processes determined that biotreatment methods were feasible and cost less than half as much as sulfide precipitation. The goal of the water treatment project was to ensure that the stringent water quality based limits in the permit would be consistently met.

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Location

The West Fork Unit is located in Reynolds County in central Missouri, about three hours from St. Louis (Figure 1). The mine is located in the New Missouri Lead Belt.

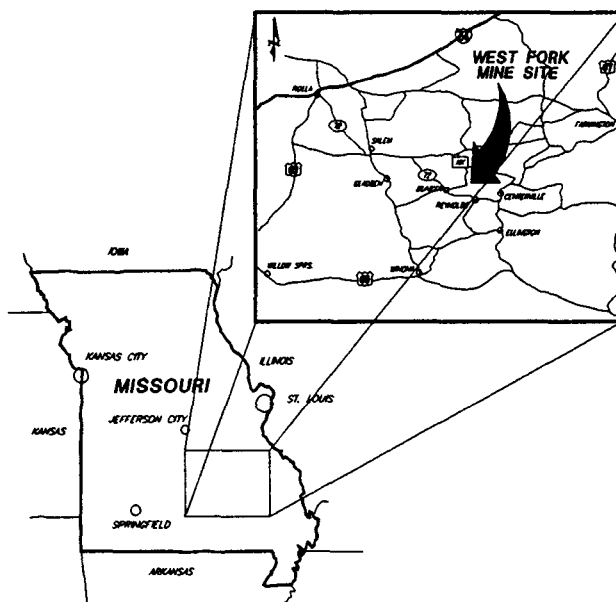


Figure 1, Site Location

Flow rates in West Fork vary from about 20 cubic feet per second (cfs) to more than 40 cfs; water quality is relatively good, despite being located in an area with naturally high background levels of lead due to the bedrock geology. The mine discharges about 1,200 gpm on the average (2.7 cfs) or about 10 percent of the total flow in West Fork.

Biotreatment

A Brief History of Biotreatment

Natural systems have been removing metals from water for eons; examples include pyrite fixed into coal beds and bog iron ore deposits. For the past 10 years, wetlands and bogs have been the natural method of choice for improving water quality. Contaminant reductions are being seen through the precipitation of hydroxides, precipitation of sulfides, and pH adjustments. Local conditions, oxidation state, and water and soil chemistries dictate whether such natural reactions occur under oxidizing (aerobic) or reducing (anaerobic) conditions. Man-made or constructed wetlands/bioreactors employ the same principles as natural wetlands, but are designed to optimize processes occurring naturally in wetland ecosystems. Aerobic and anaerobic zones occur in natural wetlands (Figure 2) (Wildeman, et al., 1993). The key goal of bioreactors/wetlands is the long term immobilization of metals in the substrate materials. Metals are precipitated as carbonates or sulfides in the bioreactor substrate (anaerobic cells) and as oxides in aerobic (rock filter) cells.

Anaerobic bioreactors have been successful at substantially reducing metal concentrations and favorably adjusting pH on metal mine drainages. It is generally

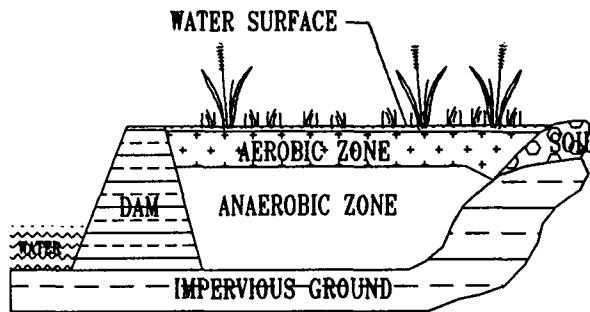


Figure 2, Natural Wetland Ecosystem Zones

recognized that the bacteria commonly found in cattle and other domestic animal intestinal tracts include sulfate reducers and a consortium of other beneficial bacteria. Hence, cow or other animal manures have been frequently used as bacterial inoculum for anaerobic biotreatment cells. These same bacteria are found in many natural wetlands and bogs, and in lakes and ocean water. Aerobic biotreatment systems are similar to "natural" wetlands in that they typically have shallow depths and support vegetation in the form of algae.

Since the early 1980's, researchers have documented water quality improvements in natural wetland systems. The former US Bureau of Mines (USBM), Tennessee Valley Authority (TVA), and universities such as the Colorado School of Mines [CSM] and others focused on plant-based ecosystems for biotreatment. Many pilot scale systems were built but results were uneven.

In the interval from 1985 to 1988, Greg Brodie of TVA and Bob Kleinmann of the former USBM began to use influent water chemistry as part of the design for aerobic type systems for treating coal mine acid rock drainage (ARD) (Hammer, 1989). In 1987, CSM, Knight Piésold/Camp Dresser & McKee and the US EPA jointly developed a pilot system for metal mine ARD at the Big Five Tunnel in Colorado. At the Big Five Tunnel, anaerobic processes were found to be important in metals removal; macroscopic ecosystems were not needed because the cells worked fine without plants.

Since 1988, there have been rapid advancements in understanding the functioning of wetland/bioreactor systems. The first large scale aerobic system (2,000 gpm capacity) was built in 1992 by TVA; the West Fork Unit system (1,200 gpm capacity) is the first large-scale anaerobic biotreatment system. Aerobic "rock filter" treatment follows for polishing manganese and other parameters.

While the volumetric flow capacity of the West Fork system is a biotreatment milestone, the metal mass loading capacity has been surpassed by many other pilot scale systems which treated water with metal concentrations one thousand times more concentrated than those observed at West Fork. The innovative West Fork technology holds promise over typical chemical treatment methods because large volumes of sludge are not generated; in fact, sludge disposal may be delayed until the end of the project life. In situ reclamation may also be feasible.

Biotreatment Removal Mechanisms

Research has shown that microbial processes are a dominant removal mechanism in anaerobic type biotreatment systems. One prominent researcher calls these systems "bioreactors with green toupees," referring to the organic substrate where most of the bioreactions occur and the collection of plants that often grow on their surfaces.

Many physical, chemical and biological mechanisms are known to occur within biotreatment systems to reduce the metal concentrations and neutralize

the acidity of the incoming flow streams. Notable mechanisms include:

- Sulfide or carbonate precipitation catalyzed by bacteria in anaerobic zones;
- Hydroxide or oxide precipitation catalyzed by bacteria in aerobic zones;
- Adsorption and exchange with plant, soil and other biological materials;
- Filtering of suspended material;
- Metal uptake into live roots and leaves; and
- Ammonia-generated neutralization and precipitation of hydroxides.

Remarkably, some studies have shown that plant uptake does not contribute significantly to water quality improvements in wetlands. This may be plant-species dependent. Plants can, however, replenish the anaerobic bioreactor with organic material and add aesthetic appeal. In aerobic biocells, plant-assisted reactions appear to aid the metal-removal performance of the system, perhaps by increasing oxygen and hydroxide concentrations in the surrounding water through photosynthesis-related reactions that use bicarbonate in the water.

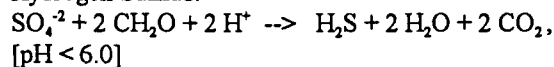
Bacterial Reactions

Research testing showed that anaerobic reactions could provide the desired level of lead remediation at West Fork. In the anaerobic systems, sulfide precipitation assisted by sulfate-reducing bacteria thriving in the anaerobic zones has been demonstrated to be the most significant metal removal mechanism. The bacterial reactions involve the generation of

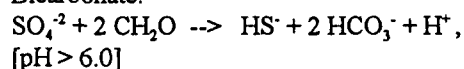
- sulfide ions (S²⁻), which combine with dissolved metals to precipitate sulfides, and
- bicarbonate, which has been shown to raise the pH or alkalinity of the effluent.

The sulfate reducing bacteria, which appear to function best above pH 5.5, are believed to produce sulfide ions which can in part volatilize into hydrogen sulfide gas (H₂S) and bicarbonate (HCO₃⁻) in accordance with the following reactions:

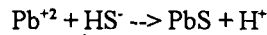
Hydrogen Sulfide:



Bicarbonate:



At low pH, hydrogen sulfide gas bubbles up through the bioreactor substrate, precipitates metals as sulfides, and essentially reverses the reactions that produced the dissolved metals in the water. At higher pH values such as those observed at West Fork, the sulfide ion is in solution and available for precipitation of metals. In the case of dissolved lead, soluble sulfide ion combines to form the lead sulfide mineral galena (PbS):



Testing had also shown that manganese in the anaerobic cell effluent was elevated during the startup period, but then it dropped below 1 mg/L after 40 days of operation. The results of testing also suggested that aerobic reactions would be required in order to polish the discharge from the proposed West Fork anaerobic cell for excess sulfide and for biological oxygen demand prior to discharge. Thus, a brief discussion of aerobic bacterial processes is appropriate.

The primary component of the West Fork aerobic biotreatment system, a "rock filter," re-oxygenates the anaerobic cell effluent as the water passes through the system and serves as a final aeration polishing pond. Excess dissolved sulfide is oxidized from the effluent solution (S²⁻ + O₂ => SO₄²⁻) in this step. Because the pH is above 7, the evolution of hydrogen sulfide gas is abated. The development of aerobic rock filters for removing dissolved organic matter that create biological oxygen demand (BOD) has been well established in municipal waste water treatment installations. The oxidizing of sulfide from anaerobic bioreactor effluent was documented from the West Fork Unit pilot scale biocell in a "sluice" installed downstream of the biocell. In the rock filter, photosynthesis reactions and open channel flows provide the oxygen needed to remove BOD and oxidize sulfide.

As the water passes through the rock filter, the combined effects of algal growth (especially in the zone surrounding the algae cell wall where pH is high) and the bacteria *Leptothrix discophora* (Robbins et al., 1997) probably precipitate most of the manganese as a black manganese oxide which coats the rocks in the rock filter. This coating is similar to the natural black coatings on rocks observed in many regional streams and ground water intersecting highway cuts throughout Reynolds County, Missouri.

Removal of manganese was projected to be required on a short term basis because its source was the substrate material in the anaerobic cells. The levels of manganese in the effluent of the pilot biocell appeared to

approach influent levels after about five months of biocell operation. Removal of manganese in rock filter aerobic cells has been documented in many studies including Wildeman, et al., 1993 and Robbins, et al., 1997.

Test Methods

As with any water treatment facility, the West Fork Biotreatment system was designed by following a phased testing approach that begins in the laboratory and progresses through bench scale and pilot scale systems before sufficient data are gathered to design a full scale passive treatment system. This approach was eventually adopted after Asarco initially constructed and operated a bench scale reactor based on a preliminary design whose results showed promise. A brief history of the design process implemented at West Fork follows.

Asarco had initiated investigations into improving water quality from the West Fork Unit into the West Fork of the Black River as early as 1989. At that time, suspended solids concentrations were the prime concern and numerous test programs were undertaken to minimize suspended solids in the effluent. While improvements were realized through modifications of settling ponds prior to discharge, effluent limits on total lead in the NPDES permit issued in October, 1991 were decreased to levels below which primary settling would work. Asarco initiated investigations into biotreatment and other treatment options to meet lead limits in early 1993 (Knight Piésold, 1995).

The investigations revealed that the unique water chemistry at the West Fork site was not amenable to "standard" water treatment techniques such as pH adjustment, flocculation/settling or sodium sulfide precipitation (which should have worked) for the removal of lead to meet effluent limits. These standard treatment processes were found to be either impractical or too expensive or could not be made to work in field tests. As such, Asarco utilized its positive experiences with biotreatment at other metal mine sites to focus on a relatively new technology that was innovative and, most important, efficient, as demonstrated by two years of pilot plant performance data.

Water quality modeling using MINTEQAQ software suggested that relatively small additions of sulfide under the anaerobic conditions of a biotreatment cell would achieve an effluent with acceptable limits for lead (less than 0.035 ppm). Other removal mechanisms such as lime or sodium carbonate additions did not meet the required treatment levels. Conversely, the biotreatment process is consistent with basic geochemical knowledge and was

confirmed by positive pilot scale test results. It was found to be the appropriate process to use to treat West Fork's unique water quality.

Bench Scale and Laboratory Testing

Evolution of the Asarco West Fork biotreatment system design began with bench scale testing. Asarco initiated biotreatment investigations in January, 1993 with the commissioning of a bench scale "bio-tank" system that was operated until February, 1994. The bio-tank, about eight feet in diameter and four feet deep, was initially filled with "green" cow manure; this substrate material was replaced in June, 1993 with a mixture of aged cow manure and aged saw dust. The bio-tank treated up to eight liters per minute (about 2.1 gallons per minute [gpm]) of mine water until it was dismantled. The undepleted substrate was then used to inoculate a larger cell.

In anticipation of pilot scale design, laboratory testing to evaluate other substrate candidate materials was undertaken in August and September, 1993. From October through November, 1993, an evaluation of the laboratory and bio-tank performance results yielded a pilot scale system design which was approved by Asarco in November of 1993. Adverse weather prevented pilot scale construction until February, 1994.

Pilot Scale Field Testing

The pilot scale system was commissioned at an outdoor site adjacent to the mine in March, 1994; it reached design flow (20 gpm) and removal rates in about June, 1994 and operated successfully at a nominal rate of about 25 gpm with flows as high as 49 gpm providing high-end operating data until February, 1996. Several polishing-type aerobic cells were added in parallel to evaluate the removal of manganese, BOD, fecal coliforms, and sulfide removal and the enhancement of dissolved oxygen in the system effluent.

Interim bench scale studies were undertaken while the pilot system was operated. These studies evaluated startup procedures to minimize BOD, fecal coliform, color, and manganese concentrations and accelerate early removal of lead in the anaerobic cell effluent.

Data from the 24-month operation of the pilot scale bioreactor showed that the biotreatment system could consistently remove total and dissolved lead to concentrations less than 0.02 ppm, despite significant fluctuations in flow and metal loading and changes in climate (rainfall and temperature).

Large Scale Design

The large scale system was designed based on the performance of the pilot scale system and the interim bench scale studies. The large scale system was estimated to cost approximately \$500,000 and require about two to three months of construction time, depending on the vagaries of weather and construction surprises. System operational costs include water quality monitoring as mandated by law. No additional costs for reagents are incurred; since the system uses gravity flow, moving parts are few and include valves, minor flow controls and monitoring devices. Based on carbon depletion rates observed in the pilot system, the anaerobic cell substrate life was projected to be greater than 30 years; the full scale biotreatment system should be virtually maintenance-free.

Should mine water quality deteriorate, the full scale design included a 50 percent safety factor. The pilot scale system was tested by operating for about 90 days at double the design capacity; compliance effluent with respect to total lead concentration and other key performance parameters resulted from this test.

Two construction sites were considered for the final system design. One site was located within the existing mine permit area, bounded by the mine/mill buildings, a pond at the toe of a tailings dam, a steep hillside, and the West Fork of the Black River, the receiving stream. This site had numerous other constraints including multiple buried utilities, a concrete-lined drainage structure which bisected the site and an above-ground liquid propane storage tank. Relocation of either of these structures was not allowed. An alternative site was located about 2,000 feet away, on the other side of the main access highway to the mine. This relatively uncluttered site consisted of open pasture land bounded by woodland on two sides, the highway, and the West Fork of the Black River. This area, while controlled by Asarco, was not within the mine permit area. Mine water to be treated would need to be pumped to this site; the pipeline would need to be bored through the highway embankment. A regional natural gas pipeline was located within the highway right of way.

After a preliminary design analysis revealed that the full scale system could fit barely within the land available adjacent to the mine/mill buildings even considering the various constraints, the alternative site was rejected to avoid additional land disturbance, permitting delays and pumping of mine effluent.

System Dimensions

The biotreatment system is composed of five major parts (Figure 3): a settling pond, two anaerobic cells, a rock filter, and an aeration pond (Knight Piésold, 1997). The system is fully lined. The design was also integrated into the mine's pre-existing fluid management system.

- A rectangular-shaped, 40 mil HDPE-lined **settling pond** has a top surface area of 32,626 square feet (0.75 acres) and a bottom surface area of 20,762 square feet (0.48 acres). The sides have slopes of 2 horizontal to 1 vertical (2H:1V). The settling pond is nominally 10 feet deep. It discharges through valves and parshall flumes into the two anaerobic cells.
- **Two anaerobic cells** are used, each with a total bottom area of about 14,935 square feet (0.34 acres) and a top area of about 20,600 square feet (0.47 acres). Each cell is lined with 40 mil HDPE and was fitted with four sets of fluid distribution pipes and three sets of fluid collection pipes, which were subsequently modified (see Start Up discussion). The distribution/collection pipes were connected to commonly-shared layers of perforated HDPE pipe and geonet materials sandwiched between layers of geofabric. This feature of the design was intended to allow control of sulfide production in hot weather by decreasing the retention time in the cell through intentional short circuiting.

The spaces between the fluid distribution layers were filled with a mixture of composted cow manure, sawdust, inert limestone, and alfalfa, referred to hereafter as "substrate." The total thickness of substrate, piping, geonet and geofabric was about six feet. The surface of the anaerobic cells was covered with a layer of crushed limestone. Water treated in the anaerobic cells flows by gravity to a compartmentalized concrete mixing vault and thereafter to a rock filter cell. The gravity-driven flows can be directed upward or downward .

- The **rock filter** is an internally bermed, clay-lined shallow cell with a bottom area of about 63,000 square feet (1.4 acres) and a nominal depth of one foot. It is constructed on compacted fill that was

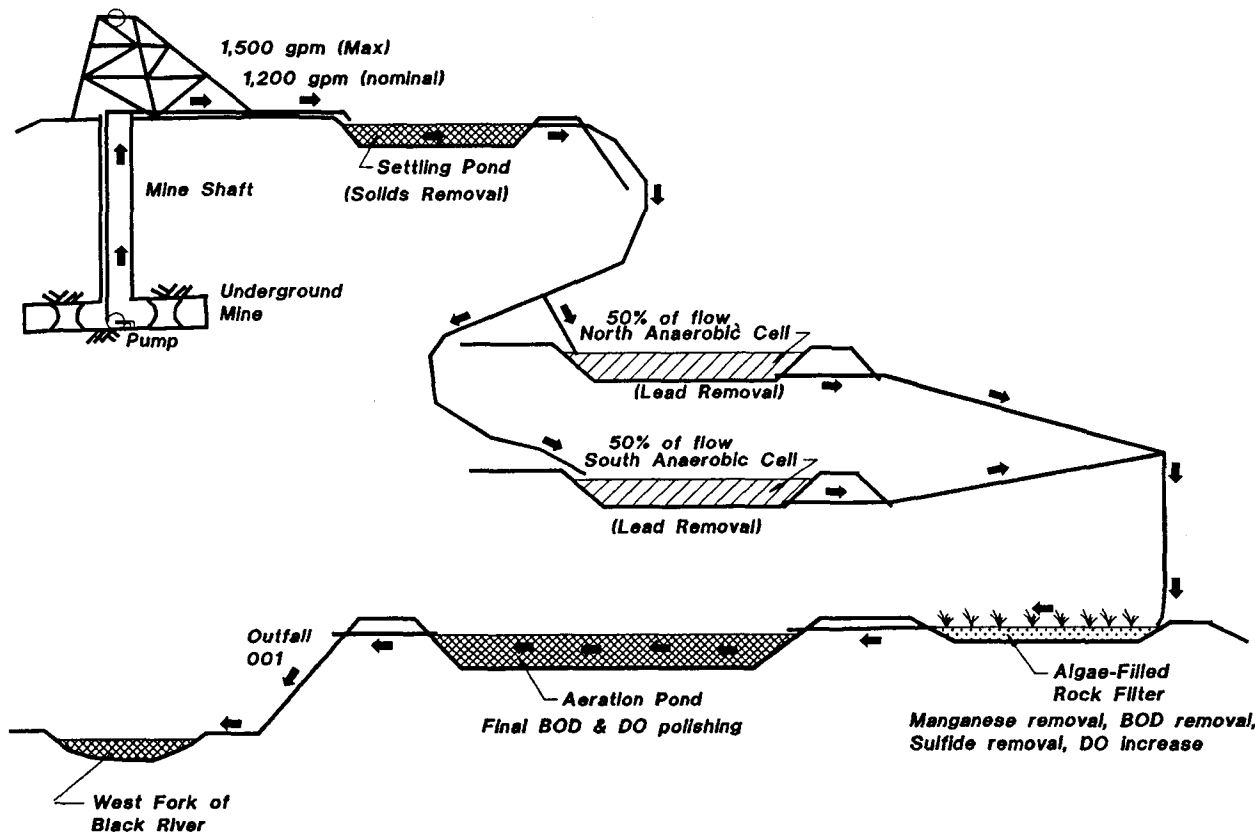


Figure 3, System Configuration

systematically placed on the west side of a pre-existing mine water settling pond. Limestone cobbles line the bottom of the cell and the cell is compartmentalized by limestone cobble berms.

- The discharge from the rock filter flows through a drop pipe spillway and buried pipe into a 40 mil HDPE lined **aeration pond**. The aeration pond surface covers approximately 85,920 square feet (2.0 acres). The aeration pond discharges through twin 12-inch HDPE pipes into a short channel that leads to monitoring outfall 001 and thence into West Fork.

After the water pumped from the underground mine enters the settling pond, all flows are by gravity.

Permitting Hurdles

The permitting aspects of the project were very complex. Regulators needed to be convinced that an organic-based wetland-type substrate could remove dissolved lead from mine effluent. Note: Missouri is known as the "Show Me" state and regulators were suspicious of a

new and innovative technique that did not quite fit in established regulatory guidelines or statutes. However, regulators were willing to listen to facts and the flow of communications was good. Nevertheless, cow manure as an ingredient in the anaerobic cell substrates was a special regulatory hurdle because its use raised issues of BOD, fecal coliform bacteria and other organic-related water quality criteria problems from a non-degradation of West Fork perspective.

From a construction permit perspective, only one regulation was a problem. Missouri Department of Natural Resources (DNR) regulation 10 CSR 20-8.110 [Engineering - Reports, Plans and Specifications] is for conventional water treatment plants that remediate fecal-type wastes. This regulation was not promulgated with the concept of using manure as a construction material.

Education of permit document reviewers was a key aspect of the permitting effort, supported by the results of the two years of pilot scale test results. The original permitting application was made after gathering one year's worth of pilot data; data acquisition continued throughout the permitting process. Making the permit submittal fit the

regulation requirements was somewhat akin to making a round peg fit into a square hole.

Missouri DNR raised useful and valid concerns which were addressed with additional testing, including monitoring for fecal coliform, color, BOD, and other minor constituents. This additional testing raised the level of knowledge of passive treatment performance in general and improved the database utilized in the final design.

The closure and reclamation of the biotreatment system after its scheduled decommissioning at the end of the West Fork facility life was also a DNR concern. The system was constructed within the boundaries of the waste management areas as defined by the Metallic Minerals Waste Management Act and was, by definition, a waste management structure. Therefore, closure and reclamation activities would adhere to Section 5 of the Metallic Minerals Waste Management Permit issued to Asarco's West Fork Unit in January, 1991.

The substrate material, made up primarily of sawdust, alfalfa hay, limestone and cow manure, was projected to accumulate metals over time through the operation of the water treatment system. Based on average flow and metal content of the mine water, it was estimated that the final metal loading in the substrate will be 1,866 mg/kg Pb as PbS. At the end of the active life of the biotreatment system, core samples of the substrate will be subjected to TCLP. If the substrate material fails TCLP, disposal will be in accordance with all applicable laws and regulations pertaining to characteristic hazardous waste. If the substrate passes TCLP, it will be used as an organic fertilizer to stimulate vegetation growth on the slope of a nearby tailings dam. Data from other sites have suggested that organic substrate containing metals will pass TCLP tests if it is allowed to oxidize first (McLain, 1995).

Odor control from the proposed facility was not expected to be a problem. Asarco personnel conducted a reconnaissance air quality screening study at the site with chemically activated sniffer sampling of air immediately adjacent to the operating pilot scale biotreatment plant. Hydrogen sulfide concentrations were the focus of the survey. Air quality modeling suggested that the facility would be in compliance with applicable standards.

Another point favoring its application at West Fork, the biotreatment method had been used at other Asarco facilities (in Colorado, Montana [which was issued an interim NPDES permit] and Canada) and it was accepted as a viable treatment method by agencies in other states and the USEPA. Some of the original research work into

biotreatment was sponsored under the EPA's Emerging Technology Program. The following mine/mill sites are known to have included biotreatment in their record of decision:

- Clear Creek, Colorado
- Buckeye Landfill, Ohio
- Palmerton Site, Pennsylvania
- Bunker Hill, Idaho

In the cases listed above, biotreatment was the preferred alternative or a key component of the preferred alternative.

System Construction

Following permitting, the biotreatment system was constructed in accordance with plans and specifications as submitted to and approved by the Missouri Department of Natural Resources (MDNR) Water Pollution Control Program. The construction was authorized under the Construction Permit issued on March 12, 1996. Work commenced on March 13, 1996; as of July 10, 1996, the work was declared to be substantially complete in accordance with the Plans and Specifications. Wet weather delayed construction in situations requiring the installation of welded geomembrane materials. There were no change orders.

Construction management of an outside contractor was provided by an Asarco engineer and construction quality assurance was conducted by a Knight Piésold engineer. Minor field changes in the design typically improved the facility. Some of these are discussed below.

The original recipe for the substrate included aged sawdust, low-manganese limestone, aged cow manure, and alfalfa hay in decreasing proportions. As specified, the alfalfa hay was assumed to be baled. A readily-available source of slightly moldy alfalfa hay cubes was substituted as a field change. The volumetric proportions of the substrate components changed slightly (the substrate became denser) and additional sawdust was used to make up the total volumetric deficit. The addition of more organic carbon could increase projected cell life, already in excess of the required operational time.

As originally designed, the anaerobic cells would have discharged via flexible hoses into geomembrane-lined channels. These were replaced by a compartmentalized reinforced concrete vault with variable-height internal baffles. This structure in essence combined the features and intent of a specified "concrete mixing vault" with the

level/flow control provided by the flexible hoses; it also took up far less space.

The construction was sequenced so that the settling pond was built and commissioned first so that the mine and mill could continue to operate during construction. Subsequently, the old settling pond was backfilled in part to become the foundation of the rock filter. The portion of the remaining settling pond was lined with HDPE geomembrane and became the aeration pond.

Start-Up Experience

Bench-scale test results suggested that the anaerobic cells be incubated with settled mine water for about 36 hours or less before fresh mine water was introduced at full flow to minimize initial levels of BOD, fecal coliform, color and manganese. For about two weeks, pumps recycled the water within the two anaerobic cells. Based on data collected in field, and subsequent laboratory confirmation, the water from the anaerobic cells was routed to the tailings pond for temporary storage. At that point, the rock filter and aeration ponds were brought on-line. In the meantime, the mine discharged according to plan through an overflow pipe from the settling pond as it had during construction of the other components. Plumbing was available to temporarily discharge to an adjacent tailings pond, if necessary, where it would be stored for later treatment and release.

After about six weeks of full scale operation, the apparent permeability of the substrate was found to be lower than expected and the system was operating nearly at capacity. The system had been designed so that either of the two anaerobic cells could accept the full flow amount on a temporary basis in case maintenance work required a complete cell shutdown.

Research found that H₂S gas, generated by the sulfate reducing bacteria, was being retained in the substrate in the anaerobic cells; this created a gas-lock situation that prevented full design flow. A temporary solution was obtained by periodic "burping" of the cells using the control valves. However, the "burping" had to be performed at 24-hour intervals and it was determined that this solution was too labor intensive.

The sulfide gas lock problem was investigated in December, 1996 by installing vent wells in the substrate and measuring the gas pressures. Observations indicated that the gas was a factor in apparent short circuiting of the water passing through the cell. The layered geotextiles, (geonet and geofabric) originally intended to promote

horizontal flow, appeared to be trapping the sulfide gas beneath them and vertical flow was being restricted. The permeability of the substrate itself was for the most part unaffected. However, construction practices in the south anaerobic cell could have contributed to the situation. Here, a low ground bearing bulldozer was used to place substrate in nominal six-inch lifts. This could have created a layering effect that may have trapped gas as well. Substrate layers in the north anaerobic cell were placed in a single lift and no layering effect was observed during subsequent excavation. It is noteworthy that the mid-cell geotextiles had not been a feature of the pilot test cell design.

The first phase of a permanent solution was implemented with a trenching machine that ripped through the geonet/geofabric layers in the south anaerobic cell. This disrupted the gas-trapping situation. Subsequently, the substrate from the entire south anaerobic cell was excavated and the cell refilled without the geotextiles in June, 1997. Identical action was taken on the north anaerobic cell in September, 1997. These actions have apparently solved the gas lock problem.

Operational Results

The average influent water quality can be compared with discharge water quality (Table 1) during the June through November, 1997 period. Discharge levels of Pb and other metals were reduced substantially from average influent levels. For Pb, the level was reduced from a typical average of 0.40 mg/L to between 0.027 and 0.050 mg/L. Zn, Cd and Cu effluent concentrations were also reduced.

Conclusions

- 1) A practical design has been developed to bring Pb values down to stringent water quality standards.
- 2) Bacterial sulfate reduction is the major Pb removal process.
- 3) An aeration step is needed to polish for Mn, BOD, fecal coliforms removal and re-oxygenation.
- 4) Pilot testing should include as many features of the final design as possible to minimize start up difficulties.
- 5) Education of regulators on innovative water treatment techniques can facilitate permit approvals.

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Table 1. West Fork Water Quality Data

Parameter	Typical Average Influent Water Quality	Range of Water Quality Discharge (June - November 1997)
Pb	0.4	0.027 - 0.050
Zn	0.36	0.055 - 0.088
Cd	0.003	<0.002
Cu	0.037	<0.008
Oil and Grease	—	<5.0
H ₂ S	—	0.011 - 0.025
Total Phosphorus	—	<0.05 - 0.058
Ammonia as N	0.52	<0.050 - 0.37
Nitrate and Nitrite	2	<0.050 - 1.7
True Color	—	10 - 15
BOD	1.7	<1 - 3
Fecal Coliform	—	<1 - 2
pH	7.94	6.63 - 7.77
TSS	—	<1 - 4.2

Sources: Asarco, Inc., 1997, and Knight Piésold LLC, 1995.

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WHY DO SOME PASSIVE TREATMENT SYSTEMS FAIL WHILE OTHERS WORK?

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ABSTRACT

There are hundreds of passive treatment systems accepting mining influenced water (MIW) throughout the world. Some systems do not perform to design expectations while others, including volunteer systems, have successfully operated relatively unattended for decades. The primary reasons for this situation include the common misconceptions that (1) a "cookbook" approach to design is valid for a wide array of MIW chemistries and site conditions, and (2) low maintenance means "no maintenance." Passive treatment systems for MIW are typically manmade ecosystems that are designed to handle a specific range of metal loading conditions and MIW geochemistry. Thus, when design conditions are exceeded, the suite of microbial to macroscopic ecosystems may be slow to recover or mature. This should be no surprise to designers. But when a particular system fails, it may be inappropriately attributed to the technology, not the design. This paper presents a standard "phased" design protocol that appears to work and provides examples of sub-par performance of selected passive treatment systems.

INTRODUCTION AND BACKGROUND

Since about 1985, wetlands and bogs have been the natural method of choice of engineers for improving water quality at many mining sites, and the number of installations continues to grow. These systems rely on common geochemical reactions that result in metal and other parameter (e.g., nitrate and cyanide) reductions.

The goal of any passive treatment design is to:

- Utilize common geochemical reactions typically assisted by locally adapted microbes or plants
- Operate without power or the addition of chemical reagents, including short-term exchange of process media
- Function without human intervention for long periods (decades)

Gusek (2000) provides a more detailed background discussion on basic passive treatment system geochemistry as well as three case histories that illustrate the wide variety of conditions in which this technology has worked. For the sake of completeness, a brief discussion of how passive treatment systems immobilize dissolved metals in MIW follows.

METALS REMOVAL MECHANISMS IN PASSIVE TREATMENT SYSTEMS

Many physical, chemical, and biological mechanisms are known to occur within passive treatment systems to reduce the metal concentrations and neutralize the acidity of the incoming flow streams. Notable mechanisms include the following:

- Sulfide and carbonate precipitation catalyzed by sulfate reducing bacteria (SRB) in anaerobic zones
- Hydroxide and oxide precipitation catalyzed by bacteria in aerobic zones

- Acidity neutralization through alkaline material dissolution
- Filtering of suspended material and precipitates
- Metal uptake into live roots and leaves
- Adsorption and exchange with plant, soil, and other biological materials

Remarkably, some studies have shown that plant uptake does not contribute significantly to water quality improvements in passive treatment systems (Wildeman, et al., 1993). However, plants can replenish systems with organic material and add aesthetic appeal.

THE DESIGN PROCESS

The design of passive treatment systems is a somewhat inexact science due to the variety of water chemistries requiring treatment and the variety of materials that can be used in construction. For chemically simple coal drainage (relatively mild pH water containing iron and manganese and little or no aluminum), engineers and scientists at the former U.S. Bureau of Mines developed "cookbook" design criteria (Hedin, et al., 1994) for aerobic systems that are still being followed (sometimes inappropriately) today. Wildeman, et al., (1993) developed a phased design protocol that is appropriate for more complex acidic as well as neutral to net alkaline drainage chemistries.

These two approaches represent end points in a design philosophy continuum. The inherent danger in any "cookbook" design approach is a typical inability to properly address situations lying outside the range of conditions that were originally used to develop the standardized design criteria. The treatment of low pH water containing dissolved aluminum is especially problematic and outside the original U.S. Bureau of Mines design criteria, which addressed the issue by suggesting restrictions in the application of anoxic limestone drains (ALDs). A precise and reliable aluminum design guideline has yet to be developed for ALDs and probably should not even be considered. That is because of the complexity of aluminum chemistry. While iron can be more or less precipitated aerobically as ferric hydroxide or anaerobically as a sulfide or carbonate, the list of aluminum mineral species found in nature (and thereby possible in a passive treatment system) is extensive.

The "cookbook" design challenge represented by the individual case of aluminum is multiplied many fold when additional heavy metal contributions are considered, as may be the case for some MIW sources at metal mines. Adding the effects of varying anionic concentrations and water temperature further reinforces the futility of considering cookbook approaches to passive treatment design. Still, the design engineer must start somewhere.

The situation is not as bleak as it may sound. Mining, chemistry, and other industries have used a phased design process, probably since the dawn of engineering. The concept is simple: start small, learn from failures, and build on successes until the data required to properly design a full-scale treatment

system are obtained. With that data, the risks of the full-scale system failure or less than optimum performance are significantly reduced. Wildeman, et al. (1993) proposed a design protocol that included laboratory-, bench- and pilot-scale phases. The approach has been used at over three dozen mine drainage sites.

A phased-approach design project typically begins in the laboratory with static tests, graduating to final testing phases (bench and pilot) performed at the site on the actual MIW. Bench-scale testing will determine if the treatment technology is a viable solution for the MIW and will narrow initial design variables for the field pilot. A proper bench-scale test will certainly reduce the duration of the more costly field pilot test. Field pilot test duration can range from days, to months, to years, depending on the nature of the technology. Depending on the nature of the equipment and personnel needed, significant costs may be incurred during the field pilot tests – about \$500 to \$1,000 per week – mostly for sampling and analysis. Compare this to \$5,000-\$10,000 per week for active treatment pilot tests. More detailed descriptions of testing phase activities follow.

TESTING PHASES

- Laboratory-scale Testing. This phase of testing is usually conducted in the laboratory. It might include:
 - Paste pH and redox testing of passive treatment material substrates
 - Static bottle tests to isolate and identify beneficial bacteria for a given cell type (aerobic or anaerobic)
 - Static limestone “cubitainer” tests for limestone consumption/alkalinity determination
- Bench-scale Testing. This phase of testing is typically performed in the controlled environment of a laboratory but can be conducted in the field. It is most appropriate for evaluating the dynamic response of different mixtures of organic substrates, system configurations, or metal loading rates. This level of testing should be relatively inexpensive to set up; most of the cost should be allocated to sampling and analysis. To keep costs down, bench-scale test units can be constructed with off-the-shelf items such as trash cans and kiddie wading pools, items typically found at do-it-yourself/home improvement stores and gardening centers. Once the range of dynamic variables has been narrowed, one should proceed to onsite pilot testing.
- Field Pilot-Scale Testing. This phase of testing is performed at the site, on the actual MIW. Information gathered during these tests should provide an accurate operating cost estimate as well as final capital cost data. If the field pilot study does not meet the necessary discharge standards, another treatment technology should be considered or added on. It is also important to determine the sludge characteristics during this phase. Will the sludge be hazardous or non-hazardous? Can the treatment sludge be disposed of on the mine site? Sludge management and organic substrate replacement may comprise the principle “operating” costs of a passive treatment system.

Upon completion of the field pilot test, full-scale design should take into consideration seasonal fluctuations in flow rate and seasonal fluctuations in chemical composition that may not have occurred during a shorter pilot test. Equalization ponds or tanks should be included in the design to handle these fluctuations.

It is important to note that there are two equally important aspects of full-scale passive treatment system design – bio-geochemistry and filtration. The bench and pilot test results should have yielded the conditions necessary to establish the proper bio-geochemistry or dominant geo-ecosystem in a given treatment cell to develop stable chemical precipitates. However, constructing an ideal bio-geochemical environment is a wasted effort if the metal precipitates formed are flushed out of the system because of inefficient filtration. Among other factors, this aspect of a proper system design is influenced by the grain-size distribution and compacted density of organic substrates, the

settling and flocculating characteristics of the precipitates, and the retention times of the settling cells.

WHY SOME SYSTEMS FAIL

There are four major reasons why some passive treatment systems do not function as intended:

- No Design, e.g., “Just build a swamp here, fill that pond over there with manure and call it good.”
- Inadequate Design. Undersized for load, applying the wrong geochemical approach, phased design lacking, complex geochemistry, improper startup and operational procedures.
- Inadequate Maintenance. (Low maintenance does not mean NO maintenance.)
- Last Minute Design Changes. Departure from well conceived construction specifications in response to field conditions can affect system performance – experience helps.

Brief discussions of these reasons follow.

Inadequate Designs

Given the wealth of technical information available in the scientific literature, it is rare to find a passive treatment system based on a “seat of the pants” design. However, without much design background, any person with a strong recollection of his or her high school chemistry can construct a system that will function successfully at some level and thus provide some proof that, yes, the concept can work in principle. This level of effort is insufficient, however, for designing a system that will work continuously for many years. Professional assistance should be sought from experienced engineers and academia to avoid frustrating failures.

Although they may be slow to admit it, professionals are not immune to failure. This is why it is prudent to:

- Experience failures and eliminate design uncertainties during laboratory, bench, and pilot testing (phased design)
- Clearly determine the range of expected metal loading (the product of flow times concentration) for the treatment situation to avoid under-sizing
- Evaluate startup procedures (being ecologically based, passive treatment systems typically should not be “turned on” at full flow; bacteria may need time to incubate or acclimate)
- Develop clear operational plans and designs that allow future maintenance without total system shutdown

A success story worthy of note, the 1,200-gpm capacity West Fork system in Missouri (see Gusek, et al., 1998 and Gusek, 2000) has met stringent NPDES permit requirements for the last five years without a single violation despite experiencing minor problems. In this case, the heart of the system was two anaerobic sulfate reducing bacteria (SRB) bioreactors, plumbed in parallel (see Figure 1). Each cell was sized (based on the results of pilot testing) to accept the full flow from the mine for up to several months in case maintenance was required.

When suspended sediment from mine hoisting operations inadvertently choked the surface of the anaerobic cells (despite an intermediate settling pond), the mine elected to replace the organic substrate with fresh materials (Murphy, 2001). This was undertaken in the summer, when bacterial activity was high, by diverting all the mine flow through one of the SRB bioreactors while the other cell was being retrofitted. The mine personnel were supported in this endeavor by an “operator’s manual” that accompanied the original plans and specifications; the original design consultant was not even contacted.

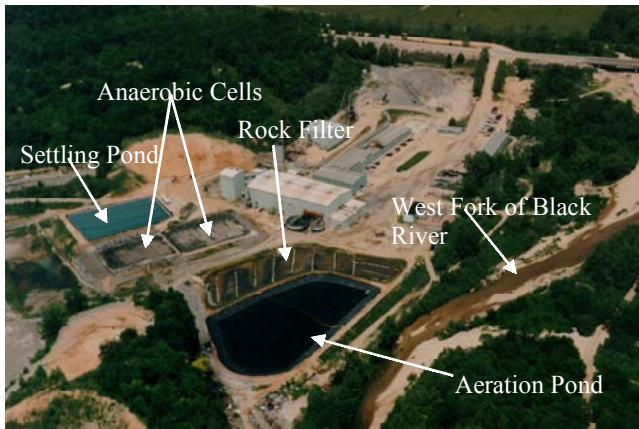


Figure 1. Aerial photo of West Fork mine passive treatment system, Missouri

Inadequate Maintenance

With minor exceptions, passive treatment systems consist of biological populations that include many suites of living things ranging from bacteria to plants. While somewhat resilient to minor, short lived changes, the biological populations in passive treatment systems cannot sustain overloading without suffering sometimes permanent damage. Overloading may not be apparent at startup. In concert with the definition of "loading" previously provided, the term "overloading" extends beyond the concept of excess flow rates (perhaps in response to storm events). It also applies to increases in metal concentration while flow remains fairly constant. Addressing this is a water management issue, solved by including surge/equalization capacity and flow controls in the system design.

Short-term changes in mineral acidity can be dealt with using limestone amendments that are periodically replenished as needed. This was a lesson that was learned at the Wheal Jane pilot system in Cornwall, England (unpublished data). An anaerobic SRB bioreactor was sized to receive flow from a series of aerobic cells (see Figure 2) that were designed based on USBM criteria to remove iron at low pH. These cells were also expected to and did remove arsenic. At the time, all flow from the aerobic cells was routed to the anaerobic cells, including direct precipitation. The prevailing thought (in 1993) was that rainfall would dilute the metals remaining and that, even at increased flow rates, the loading would stay constant. However, a number of conditions combined to overwhelm the SRB cell receiving the effluent from the aerobic cells. First, the aerobic cells were not as efficient as expected in neutralizing mineral acidity, and rainfall dilution did not significantly affect the mineral acidity of the water, a critical design parameter for SRB cells. Second, overloading occurred during the winter when SRB bacteria activity was stressed already due to the low water and air temperatures. Third, and lastly, the organic substrate did not contain any inherent buffering capacity (bench-scale tests had not been performed due to schedule restrictions). In summary, the stressed SRB were hit with an acidity overload, and there was no self-buffering component in the substrate to counter it. Consequently, the metal removal performance of the cell suffered. Fortunately, this was a pilot test, and the situation was corrected by excavating the anaerobic substrate, amending it with limestone, re-inoculating with manure, and installing a flow restriction device (orifice) on the aerobic cell outfall that helped to manage the flow peaks. The cell responded favorably and was subsequently more successful at zinc (and iron) removal.



Figure 2. Aerobic cell at the Wheal Jane Mine, Cornwall, UK

Another similar situation occurred at the Burleigh Tunnel in Colorado (EPA, 1999), but the outcome was different. This drainage typically has neutral pH and about 50 to 60 mg/L of dissolved zinc. Two pilot-scale cells, each capable of handling about 7 gpm (see Figure 3), were constructed in 1994. Like the Wheal Jane SRB cells, the Burleigh Tunnel SRB cells were exposed to a high flow/high concentration event (pH 4.1 [estimate], Zn at 109 mg/L, and flow at 20 gpm – loading was estimated to be three times the design rate) in 1995 in response to the spring snowmelt. The acidity loading also increased, and despite some self-buffering capacity of the substrate, the cells' performance suffered. Unlike the test protocol at Wheal Jane, there was no intervention response to the overloading event such as reducing the flow to allow the SRB to recover or re-inoculation with fresh SRB. Consequently, the cells limped along for another year before the test was terminated. In the view of this author, the results of this test could have been markedly different (and more positive) had some effort at system maintenance been made.



Figure 3. Burleigh Tunnel pilot-scale cell, Silver Plume, Colorado

Last Minute Design Changes

As stated earlier, a properly designed passive treatment system should be based on a phased testing program of laboratory-, bench-, and pilot-scale experiments. These experiments and the subsequent design must take into account the physical availability of some construction materials. Bench testing may have identified a superior type of organic component that the SRB favored, but it may not be available in sufficient quantities to warrant including it in the final design. Local farmers in particular are notorious for offering to give away animal manure

SUMMARY

Passive treatment technology has been proven to be effective in a variety of geochemical, flow, and climatic situations (Gusek, 2000). However, "cookbook" design approaches should be implemented on a full-scale basis with caution; it would be more prudent to use cookbook designs as a starting point for bench- or pilot-scaled passive treatment systems. Conclusively, many system failures can be avoided by using phased testing of system designs and attention to detail during construction, operation, and maintenance.

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during the testing phase of the project only to boost the price to capitalize on a captive market when large quantities need to be procured. Contractors and project owners seek relief from these situations by substituting "similar" but less expensive sources which are virtually the same. Again, the West Fork Project in Missouri provides a couple of instances where minor digression from the pilot design caused subsequent problems in the full-scale system.

As reported in more detail by Gusek (2000), the first problem related to the use of geotextile in the organic substrate column, which was 6 feet (2.9 meters) thick in both the pilot and final design. To allow better flow control/system throttling in the full-scale SRB cells during the summer, intermediate layers of perforated pipes were installed in the substrate at the 2-foot and 4-foot depths. To facilitate water collection/dispersion, the pipes were sandwiched between a layer of geonet and two layers of geotextile. Due to project scheduling, there was not time to test this concept on a pilot scale; the design change appeared to be minor. Another minor design change occurred during construction of the full-scale system. Alfalfa hay that was used in the construction of the pilot was in short supply; a source of spoiled alfalfa pellets was offered as a substitute and approved by the field engineer.

The two combined changes above had significant impacts on the ultimate hydraulic performance of the SRB cells. While the geochemical characteristics of the substrate mix met the design specifications, the physical situation caused by the changes was a significant departure from the pilot design. First, the geotextile trapped some of the gases evolved from the biological activity and created a "gas-lock" condition that restricted fluid flow through the cell. Second, the substitution of the alfalfa product in place of the baled source yielded a substrate with a slightly lower saturated permeability than that measured in the pilot. The net result was a system that was geochemically sized to temporarily treat elevated flows, but the flow restrictions prevented this design feature of the system from being used. The condition was ultimately fixed, but a valuable lesson was learned. Even minor deviations from bench- or pilot-scale configurations or design can result in major changes in system performance and should be avoided as much as possible.

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REALITY CHECK: PASSIVE TREATMENT OF MINE DRAINAGE AN EMERGING TECHNOLOGY OR PROVEN METHODOLOGY?

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ABSTRACT

Passive treatment of mine drainage using constructed wetlands has been employed on coal and metal mine sites since about 1985. The technology has advanced significantly since then; there are currently over 600 of these systems treating coal mine drainage in the Eastern U.S. at flow rates of hundreds of liters per minute. Passive treatment performance at three metal mines discussed in this paper has been positive for a wide variety of flows, water chemistry, and climates. The sites include a high-altitude underground copper mine, acidic seepage from a gold heap leach pad, and pumped effluent from an active underground lead mine in Missouri.

INTRODUCTION AND BACKGROUND

Natural systems have been removing metals from water for eons; examples include pyrite fixed into coal beds and bog iron ore deposits. For the past dozen years, wetlands and bogs have been the natural method of choice for improving water quality. Contaminant reductions are being seen through the precipitation of hydroxides, precipitation of sulfides, and pH adjustments. Local conditions, oxidation state, and water and soil chemistries dictate whether such natural reactions occur under oxidizing (aerobic) or reducing (anaerobic) conditions. Man-made or constructed wetlands/bioreactors employ the same principles as natural wetlands but are designed to optimize processes occurring naturally in wetland ecosystems. The key goal of bioreactors/wetlands is the long-term immobilization of metals in the substrate materials. Metals are precipitated as carbonates or sulfides in the bioreactor substrate (anaerobic cells) and as oxides and hydroxides in aerobic (rock filter) cells.

Anaerobic bioreactors have been successful at substantially reducing metal concentrations and favorably adjusting pH on metal mine drainages. It

is generally recognized that the bacteria commonly found in cattle and other domestic animal intestinal tracts include sulfate reducers and a consortium of other bacteria. Hence, cow or other animal manures have been frequently used as bacterial inoculum for anaerobic biotreatment cells. These same bacteria are found in many natural wetlands and bogs and in lakes and ocean water. Aerobic biotreatment systems are similar to "natural" wetlands in that they typically have shallow depths and support vegetation in the form of algae and emergent plant species.

Since 1988, there have been rapid advancements in understanding the functioning of wetland/bioreactor systems. The first large-scale aerobic system (7.6 cu m per min or 2,000 gpm capacity) was built in 1992 by TVA in Alabama; the West Fork Unit system (4.5 cu m per min or 1,200 gpm capacity) was constructed in Missouri in 1996 and is the first large-scale anaerobic biotreatment system. At West Fork, an aerobic "rock filter" cell provides polishing treatment for manganese and other parameters.

The passive treatment technique holds promise over typical chemical treatment methods because large volumes of treatment residuals are not generated; in fact, residual disposal may be delayed for decades or longer. One volunteer passive treatment system outside an abandoned metal mine that has operated unattended since about 1889, over a century (Beining and Otte, 1997), has been identified in Ireland. This volunteer passive treatment system reportedly has 70 percent of its total metal removal capacity remaining.

Metals Removal Mechanisms in Passive Treatment Systems

Many physical, chemical, and biological mechanisms are known to occur within passive treatment systems to reduce the metal concentrations and

neutralize the acidity of the incoming flow streams. Notable mechanisms include:

- Sulfide and carbonate precipitation catalyzed by sulfate-reducing bacteria (SRB) in anaerobic zones
- Hydroxide and oxide precipitation catalyzed by bacteria in aerobic zones
- Filtering of suspended material
- Metal uptake into live roots and leaves
- Ammonia-generated neutralization and precipitation
- Adsorption and exchange with plant, soil, and other biological materials.

Remarkably, some studies have shown that plant uptake does not contribute significantly to water quality improvements in passive treatment systems (Wildeman, et al., 1993). However, plants can replenish systems with organic material and add aesthetic appeal. In aerobic systems, plant-assisted reactions appear to aid overall metal-removal performance, perhaps by increasing oxygen and hydroxide concentrations in the surrounding water through photosynthesis-related reactions and respiration in the plant root zone. Plants also appear to provide attachment sites for oxidizing bacteria/algae. Research has shown that microbial processes are a dominant removal mechanism in passive treatment systems (Wildeman, et al., 1993). One anonymous researcher considered a passive treatment system as a "bioreactor with a green toupee," referring to the substrate where most of the bioreactions occur and the collection of plants that grow on top of the treatment cells.

Typical Conditions for Using Aerobic Systems

For slightly acidic (pH greater than 5.5) acid rock drainage (ARD) without excessive dissolved iron concentrations, hydroxide and oxide precipitation catalyzed by bacteria may be utilized as the dominant removal mechanism. Aerobic systems are similar to "natural" wetlands in that they typically have shallow depths. For the same level of treatment capacity, aerobic systems typically require larger areas than anaerobic systems. This can be an important design consideration if land availability is an operational constraint. Aerobic systems have been used to treat coal mine drainages at 17 of TVA's mine and coal washing plant sites in Alabama and Tennessee (Wildeman, et al., 1993). When the pH of the drainage is greater than 5 and iron is less than 50 mg/L, effluent quality consistently meets off-site discharge criteria. While some metal mine drainage can also have pH values above 5.5, aro-

bic reactions typically cannot raise the pH high enough to efficiently remove heavy metals such as copper, lead, zinc, nickel, and cadmium. However, aerobic systems are effective at removing iron and manganese.

Typical Conditions for Using Anaerobic Systems

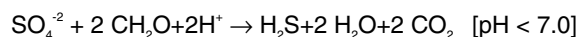
Anaerobic systems, sometimes referred to as "compost" systems, can raise pH and reduce dissolved metals concentrations in an anaerobic geochemical environment developed by the controlled decay of organic matter. The "compost" name is somewhat a misnomer, for experience has shown that *composted* organic matter is a relatively poor long-term SRB nutrient source for anaerobic systems. The composting process consumes much of the beneficial organic material needed for the process to work over the long term.

For very acidic waters (pH less than 5.5), sulfide precipitation assisted by SRB thriving in anaerobic zones in the wetland substrate has been demonstrated to be the most significant metal removal mechanism. The SRB reactions involve the generation of:

- *Sulfide ion* (S^{2-}), which combines with dissolved metals to precipitate sulfides
- *Bicarbonate* (HCO_3^-) which has been shown to raise the pH of the effluent.

The SRB, which appear to function best above pH 5.0, are believed to produce hydrogen sulfide gas (H_2S) and bicarbonate (HCO_3^-) in accordance with the following reactions (Wildeman, Brodie, and Gusek, 1993):

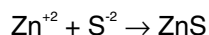
Hydrogen sulfide/carbon dioxide:



Sulfide ion/bicarbonate:



The hydrogen sulfide gas, bubbling up through the wetland substrate or occurring as the dissolved sulfide ion, precipitates metals as sulfides, essentially reversing the reactions that occurred to produce ARD. For example, the following reaction occurs for dissolved zinc, forming amorphous zinc sulfide (ZnS):



The key conditions for SRB health are a pH of 5.0 (maintained by the SRB itself through the bicarbonate reaction), the presence of a source of sulfate (typically from the ARD), and organic matter ($[CH_2O]$ from the substrate). Anaerobic wetlands and bioreactors have been successful at substantially

reducing metal concentrations and favorably adjusting pH of metal mine drainages.

WORKING SYSTEM CASE HISTORIES

Knight Piésold has been involved with about two dozen ARD and mine water remediation projects, some of which have resulted in the construction of large-scale systems. Discussion of selected results from three of these sites follows.

Brewer Gold Mine, South Carolina

This open pit gold mine (which has since been closed) had two ARD sites, a flooded open pit and a spent cyanide heap leach pad. Two anaerobic pilot cells were built. The cells were filled with a mixture of composted turkey manure, sawdust, phosphate rock reject (limestone), and cow manure SRB inoculum. The cells treated 3.8 and 2.8 L per min (1.0 and 0.75 gpm) (pit and pad flows, respectively) for approximately 18 months. This discussion focuses on the treatment of spent heap leach pad (Pad 5) effluent. The pad had been rinsed to reduce cyanide concentrations, but its effluent had turned acidic.

A 0.73 m (2.4 ft) deep, 372 sq m (4,000 sf) anaerobic cell was commissioned in early September 1993 and operated by mine personnel who were instructed to minimize ponding on the cell surface to preclude iron hydroxide formation. As discussed below, Pad 5 effluent water chemistry varied considerably during the experiment, showing the resilience of passive treatment in this respect. In fact, the Pad 5 Cell was originally designed for a flow of 19 L per min (5 gpm), but by the time the system was commissioned, influent water chemistry had deteriorated so that the flow was reduced to 50 percent of the design value to prevent overwhelming the cell's biochemistry. Cell dimensions were determined by balancing the estimated volumetric sulfate-reducing capacity (about 0.3 moles of sulfate reduced per day per cubic meter of substrate) with the molar loading of dissolved metals. The surface area was based on positive experience at other sites (20 sq m per L per min or 800 sf per gpm) with similar water chemistry.

Throughout the testing program, Pad 5 influent concentrations fluctuated in response to rainfall events on the heap and the presumed rise of pyrite oxidation activity as buffering leach solutions were rinsed out. Iron concentration varied from 8 mg/L after a leach solution flush to about 3,950 mg/L at decommissioning. Key metals concentration, metals removal efficiency, and field data gathered during the Pad 5 Cell operation are graphically shown in Figures 1 and 2 which detail:

- Metal removal performance on a percent-age-of-influent basis

- Influent and effluent pH field measurements and flow rate into the cell
- Redox/Eh field observations
- Total iron removal performance
- Total aluminum removal performance
- Total copper removal performance.

Right after start-up, volunteer vegetation invaded the cell surface, marking the "vegetation flourishes" period of the cell history. The cell vegetation was intentionally suppressed in two subsequent events and the cell refitted with a fresh source of native hay before the system was decommissioned in February 1995 to accommodate ongoing reclamation/closure activities.

As shown on Figure 1, after the start-up period until June 1994 (the "vegetation flourishes" period), the Pad 5 Cell had erratic metal removal performance. The redox/Eh during this time was erratic, which was in concert with the metals removal with the exception of iron, which was nearly 99 percent removed. Copper removal was particularly erratic; at times, copper in the effluent exceeded influent values, that is, copper was being remobilized. Aluminum removal paralleled copper values but never exceeded influent concentrations. Remarkably, effluent pH remained around the 6.5 value during this time despite large variations in influent pH due to leach solution being flushed from the heap after storm events or earthmoving activities.

The high redox/Eh values and other observations (e.g., effluent temperatures higher than 10°C) prompted the intentional elimination of the Pad 5 surface vegetation in June 1994, beginning the post-vegetation I period. Immediately thereafter and until the vegetation was again intentionally eliminated on October 27, 1994 (beginning of the post-vegetation II period), the percentage of aluminum, copper, and iron removed became steadier and more consistently in the range between 95 percent and 100 percent.

As shown on Figure 2, influent metal concentrations began to increase at the beginning of the post-vegetation I period and increased steadily until decommissioning. Iron in particular increased to about 3,950 mg/L, over an order of magnitude higher than the design concentration or the initial influent concentration. Remarkably, metals removal in the cell kept pace, especially during the post-vegetation II period as shown on Figure 2 for aluminum, iron, and copper. Flow was maintained at about 2.8 L per min (0.75 gpm) because it was difficult to adjust it any lower. As shown on Figure 1, pH in the effluent decreased from 6.5 to 6.0 during

the post-vegetation I period, which prompted the second intentional defoliation event. Toward the last month of the post vegetation I period, the removal percentage of aluminum began to drop below 50 percent, corresponding to a drop in iron removal. This change prompted another vegetation elimination.

The vegetation was again eliminated on October 27, 1994. From this time to the decommissioning of the Pad 5 Cell, copper, iron, and aluminum removal were consistently very near 100 percent. The effluent pH was observed to maintain a value of around 6.5. Sulfate influent and effluent differences increased even more markedly than in the post-vegetation I period. Remarkably, permeability of the organic substrate appeared to be unaffected by the elevated aluminum concentrations in the influent; aluminum tends to form a gel-like hydroxide precipitate which plugs limestone-dominated SAPS units used to treat coal mine drainage after a few months of operation (Kepler, et al., 1997).

Brewer Pad 5 Conclusions: After start-up, this cell removed metals using oxidation reactions promoted by the plants on the cell surface; the limestone in the substrate probably assisted by buffering the iron hydrolysis reactions. This is supported by the excellent iron removal efficiency and the poor-to-negative removal efficiency for copper.

Once the vegetation was removed the first time, anaerobic SRB-fostered reactions returned as the dominant removal mechanism. This is supported by the low redox/Eh, the marked improvement in metals removal, and observed increases in sulfate reduction.

After the second defoliation, sulfate reduction exceeded design expectations which allowed the cell to continue to function despite the order of magnitude increase in metal loading, most notably iron. The sulfate reduction peaked at a rate of over 2.0 moles/day/cubic meter; it is suspected that this phenomena would not have continued had the cell been operated for a few more months. The higher than expected rate was likely related to the readily digestible source of carbon provided by the recently killed vegetation. The root and stem tissues of the dead plants appeared to provide a superior nutrient carbon source compared to the hard wood cellulose (sawdust) tissues already present in the substrate. The hay that had been added to the cell during retrofit probably functioned in the same manner. This is consistent with reports of others (Tsukamoto, et al., 1997) using ethanol as an organic source.

A carbon mass balance analysis was conducted with the available data. During the period when vegetation flourished, the carbon necessary for cell

operation was low because of the predominance of aerobic reactions. After the successive defoliations and as sulfate reduction became the predominant bio-geochemical reaction in the cell, carbon utilization by metal precipitation reactions and sulfate reduction tracked each other remarkably well. That is, all carbon needed for metals removal appeared to be derived from the hard wood substrate and the recently killed plants.

If live, green plants were not so detrimental to cell performance, say with a deeper cell, it appears that sulfate reduction rates could be maintained at the design rate of 0.3 moles/day/cubic meter. The organic matter from the plants might provide a "balanced" diet for sulfate reducers, allowing both easily digestible plant tissues to compliment the "roughage" provided by the hard wood substrate component. With a deeper cell, surface vegetation may provide a small component to prolong cell life although total long term self-sufficiency may not be feasible, i.e., the cell would have a finite life governed by initial SRB-available carbon levels.

Ferris-Haggarty Mine/Osceola Tunnel, Sierra Madre Mountains, Wyoming

This high-elevation 2,900 m (9,500 ft) abandoned underground copper mine has neutral pH discharge with 3 to 20 mg/L dissolved copper and low sulfate (typically less than 100 mg/L SO₄); water temperature is close to freezing ($\pm 4^{\circ}\text{C}$), and the mine is accessible only by a 32-km (20-mile) snowmobile trek for nine months out of the year. Flow from the portal varies from 57 to 114 L per min (15 to 30 gpm) in the winter months to 1.7 cu m per min (450 gpm) or more during the spring runoff. Copper concentration initially observed at the portal was fairly constant all year long, somewhat independent of flow rate. However, since the completion of tunnel rehabilitation activities, a spike of elevated copper concentration and low pH (3.8) was observed coincident with the spring freshette.

The first of two pilot-scale passive treatment cells was composed of a single gravity-fed anaerobic SRB-cell configured in a downflow mode. In the summer of 1997, a 4.6-m (15-ft) diameter and 1.2-m (4-ft) deep cell was filled with a mixture of softwood sawdust, hay, limestone, cow manure, and gypsum. The proportions in the recipe were selected based on a six-week-long bench-scale (trashcan-size) test conducted in the summer of 1996. Results of a second pilot-scale cell constructed in the summer of 1999 are not available. The discussions that follow deal solely with the *first* pilot cell.

Due to the low mine water temperature, the initial slug of water used in incubation was heated to about

15°C. The cell was incubated for about a week before it received full design flow of 19 L per min (5 gpm) at about 3EC. The cell had been fully operational since early September 1997. Snow depths on site can reach 3 m (10 ft) over a typical winter season. The pilot cell was enclosed in a shed to allow winter access for sampling, inspection, and data retrieval.

Geochemical activity in the underground mine itself provides some metals remediation; not all the metal loading observed underground is accounted for at the tunnel portal. Seasonal flow from underground ore chutes exhibits low pH (3.8), elevated copper (30 to 50 mg/L), and some ferric iron. The principal ore involved in this ARD generation is suspected to be chalcopyrite. The ARD from the ore chutes (chute/shaft water) appears to mix with relatively pristine groundwater entering the furthest in-by portions of the mine and other fresh water infiltration sources closer to the portal. Under certain conditions, copper carbonates and silicates precipitate as a green or blue-green sludge on the floor of the tunnel. This geochemical phenomenon acts to remediate copper loading at the portal during a portion of the year. However, the accumulated sludge acts both as a sink and a source for copper loading at the portal; at other times of the year, copper loading at the portal was greater than that observed at the ore chutes. It is suspected that the sludge was redissolving in response to shifts in geochemical equilibrium of the mine water. Since the tunnel was reopened and the floor of the tunnel was mucked out, this source/sink phenomena has been somewhat suppressed.

The pilot cell was designed based on an estimated sulfate reduction rate of 0.15 moles/day/cubic meter of substrate, the value that was observed in the best cell in the 1996 bench-scale study. This results in a retention time in the cell of less than 12 hours.

The pilot cell was outfitted with an ISCO 6700 automatic sampler and a YSI probe to monitor pH, conductivity, redox potential, and water temperature in late October 1997, just prior to a blizzard that effectively ended the short field season. No heat-trace equipment was installed; all pipes carrying water were buried and/or fitted to maintain flow to prevent freezing.

Bi-monthly site visits via snowmobile were conducted during the winters of 1997/98 and 1998/99 to collect data and samples. Monthly sampling was conducted during the summers of 1998 and 1999. During the winters, sub-freezing air temperatures resulted in an ice covering over about 40 percent of the cell surface. Flow through the cell decreased from an initial value of 19 L per min (5 gpm) in

October 1997 to about 11.4 (3 gpm) in the subsequent months.

A number of physical and chemical parameters were evaluated for the pilot-scale cell from start-up in August 1997 through June 1999 in order to evaluate the efficiency of the pilot-scale cell. Parameters discussed in this paper include copper removal, pH, sulfate reduction, redox potential, temperature, and saturated hydraulic conductivity.

Figure 3 (Reisinger, et al.) shows total copper removal for the pilot-scale cell. Copper removal during the first nine months of operation (that is, from August 1997 through May 1998) ranged from 95 to 100 percent. Once more highly contaminated chute/shaft water (from deeper in the mine) was introduced in June 1998, copper removal efficiencies decreased to generally between 89 to 97 percent. The removal efficiencies noted during December 1998 (84 percent) and May 1999 (63 percent) were likely due to system upsets caused by contaminated water not being fed to the cell.

As shown in Figure 3, the pH of the processed water remained relatively neutral even with a change in feed waters from relatively neutral pH (Osceola Tunnel portal water) to a pH ranging from about 3.5 to 4.0 (chute/shaft water). Both the SRB and limestone incorporated into the substrate recipe likely contributed to the ability of the cell to maintain a relatively neutral pH.

Sulfate reduction is an indication of the level of SRB activity. The greater the sulfate reduction, the more the SRB activity. During the first several months of cell operation, sulfate reduction was not apparent and was likely masked by the addition of gypsum into the substrate recipe. Gypsum addition was done to enhance the cell environment for the SRB during system start-up. After the first several months, the cell generally exhibited sulfate reduction, especially during the period when higher sulfate-containing chute/shaft water was being processed.

Figure 3 also shows Ev measurements for pilot cell inflow and discharge. Ev is a measure of redox potential. The more positive the Ev value, the more oxygen-enriched the water. The more negative the Ev value, the more oxygen-deprived the water. Ev values for processed water in the range of -200 millivolts (mv) or lower suggest an anaerobic environment. As can be seen in Figure 3, Ev values are generally below -200 mv with the exception of the positive value observed during June 1999. This value is likely due to the cell not processing water at the time of the site visit.

One of the challenges of the project was the near-freezing temperature of the water requiring treatment. Temperatures of processed water ranged from about 1° to 8°C (34° to 46°F). Previous researchers (Kuyucak, 1991) suggested that sulfate-reducing reactions are not efficient enough at low temperatures (less than 10°C) to make passive treatment practical in winter conditions. However, others (Postgate, 1979) observed SRB in sub-freezing situations (from +4° to -40°C) in sea water in Antarctica. Pilot-scale data suggest that the SRB can function at the design activity rate at water temperatures approaching less than 1°C as recorded by an automated temperature probe at the pilot-scale cell discharge.

Conclusions: A pilot-scale passive treatment test conducted at the Ferris-Haggarty site over two years suggests the viability of removing copper using passive treatment techniques at near-freezing temperatures. Pilot-scale passive treatment testing will continue at the site into summer 2000; a full-scale system is planned for construction in the future. In August 1999, a second pilot-scale cell was constructed with a slightly different substrate mixture and buried to more closely mimic the planned full-scale system. The advantage of low maintenance requirements for passive treatment make passive treatment attractive compared to other more active technologies, especially at remote sites such as Ferris-Haggarty.

Doe Run Company, West Fork Unit, Missouri

This operating underground lead mine has a neutral pH discharge with 0.4 to 0.6 mg/L lead and 0.36 mg/L zinc; flow is about 4.5 cu m per min (1,200 gpm). The large-scale system was designed based on the performance of a pilot-scale system and interim bench-scale studies. Including engineering and permitting, the large-scale system cost approximately \$US700,000 (Gusek, et al., 1998) and required about four months to construct. System operational costs included water quality monitoring as mandated by law. No additional costs for reagents were incurred; since the system uses gravity flow, moving parts are few and include valves, minor flow controls, and monitoring devices. Based on carbon depletion rates observed in a pilot system, the anaerobic cell substrate life was projected to be greater than 30 years; the full-scale biotreatment system should be virtually maintenance-free. Should mine water quality deteriorate, the full-scale design included a 50 percent safety factor. The pilot-scale system of 95 L per min (25 gpm) was tested by operating for about 90 days at double the design capacity; compliance effluent with respect to total

lead concentration and other key performance parameters resulted from this test.

The biotreatment system is composed of five major parts: a settling pond, two anaerobic cells, a rock filter, and an aeration pond (Gusek, et al., 1998). The system is fully-lined. The design was also integrated into the mine's pre-existing fluid management system. A rectangular-shaped, 40-mil HDPE-lined settling pond has a top surface area of 3,030 sq m (32,626 sf) and a bottom surface area of 1,930 sq m (20,762 sf). The sides have slopes of 2 horizontal to 1 vertical (2H:1V). The settling pond is nominally 3 m (9.8 ft) deep. It discharges through valves and parshall flumes into the two anaerobic cells.

Two anaerobic cells were used, each with a total bottom area of about 1,390 sq m (14,935 sf) and a top area of about 1,930 sq m (20,600 sf). Each cell was lined with 40-mil HDPE and was fitted with four sets of fluid distribution pipes and three sets of fluid collection pipes. The distribution/collection pipes were connected to commonly shared layers of perforated HDPE pipe and geonet materials sandwiched between layers of geofabric (which were subsequently removed). This feature of the design was intended to allow control of sulfide production in hot weather by decreasing the retention time in the cell through intentional short-circuiting.

The spaces between the fluid distribution layers were filled with a mixture of composted cow manure, sawdust, inert limestone, and alfalfa, referred to hereafter as "substrate." The total thickness of substrate, piping, geonet, and geofabric was about 2 m (6 ft). The surface of the anaerobic cells was covered with a layer of crushed limestone. Water treated in the anaerobic cells flowed by gravity to a compartmentalized concrete mixing vault and thereafter to a rock filter cell. The gravity-driven flows can be directed upward or downward.

The rock filter is an internally-bermed, clay-lined shallow cell with a bottom area of about 5,900 sq m (63,000 sf) and a nominal depth of 30 cm (1 ft). It is constructed on compacted fill that was systematically placed on the west side of a pre-existing mine water settling pond. Limestone cobbles line the bottom of the cell, and the cell is compartmentalized by limestone cobble berms. The discharge from the rock filter flows through a drop pipe spillway and buried pipe into a 40-mil HDPE-lined aeration pond. The aeration pond surface covers approximately 8,000 sq m (85,920 sf). The aeration pond discharges through twin 30-cm (1-ft) diameter HDPE pipes into a short channel that leads to monitoring outfall 001 and thence into West Fork.

After the water pumped from the underground mine enters the settling pond, all flows are by gravity.

Wildeman, et al. (1998) theorized from sulfate-reducing stoichiometry that carbon depletion would be the most likely factor limiting the operational longevity of an anaerobic substrate. Simultaneous alkalinity and sulfate reduction values were used to independently estimate carbon consumption rates (and cell life span) in West Fork Unit substrate. A carbon balance analysis revealed a projected cell longevity (about 80 years) consistent with early estimates by Wildeman, et al.

West Fork Operations Results: Since start-up, the system discharge has met permit requirements. Discharge levels of lead and other metals were reduced substantially from average influent levels. For lead, the level was reduced from a typical average of 0.50 mg/L to between 0.027 and 0.050 mg/L; zinc, cadmium and copper effluent concentrations were also reduced. The following conclusions were reached as a result of completing this landmark project:

1. A practical large-scale anaerobic design has been developed to bring lead values down to stringent water quality standards.
2. Bacterial sulfate reduction is the major lead removal process.
3. An aeration step is needed to polish for manganese, biological oxygen demand, fecal coliform removal, and re-oxygenation.
4. Pilot testing should include as many features of the final design as possible to minimize start-up difficulties.
5. Education of regulators on innovative water treatment techniques can facilitate permit approvals.

SUMMARY

The three case studies provide a broad spectrum of water flow rates, metal mine drainage chemistry, and environmental conditions where passive treatment systems can work. In conclusion, the passive treatment of ARD holds much promise, especially for the chronic, low flows or loadings associated with mine and mill site drainages that nag the closure and reclamation processes. Hurdles still remain in completely understanding and designing for the biochemical and geochemical reactions that occur in passive treatment systems. However, the performance data available from the three sites considered in this paper appear to be consistent among the group and with the results of previous work collectively support the author's assertion that the technology has progressed toward becoming a "proven methodology" for treating ARD.

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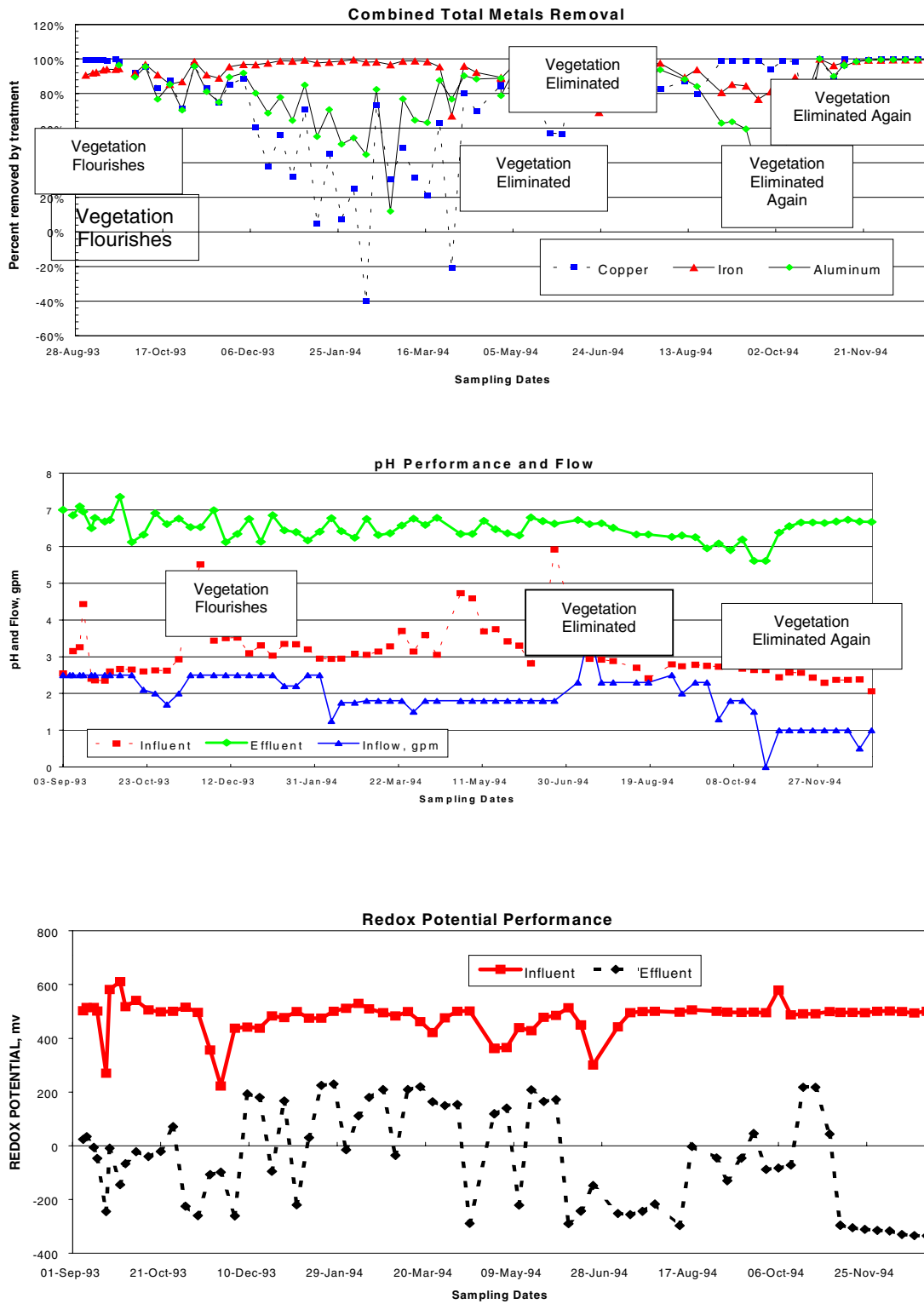


Figure 1. Brewer Pilot Passive Treatment Results.

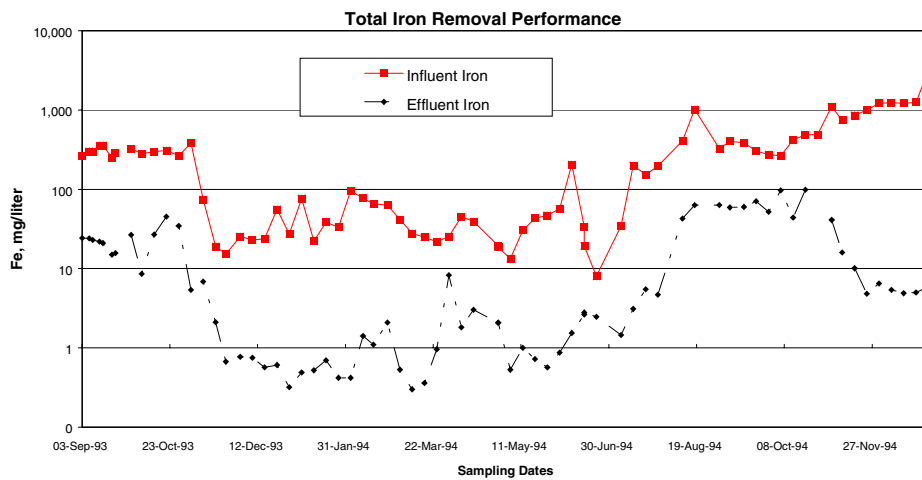
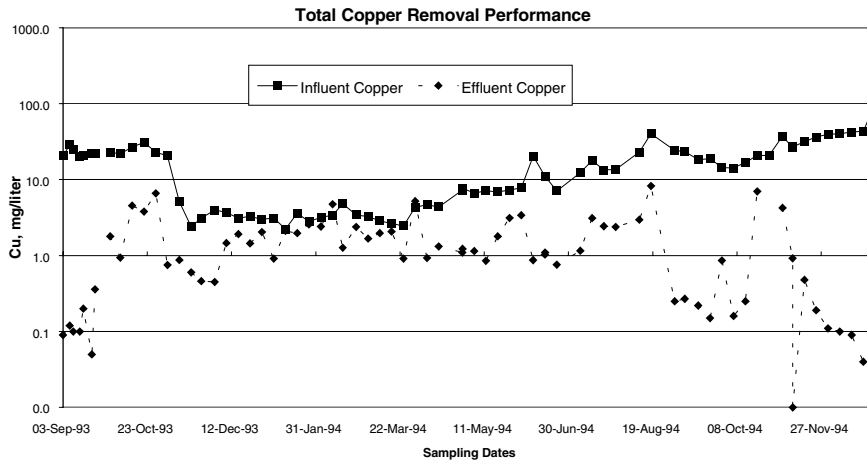
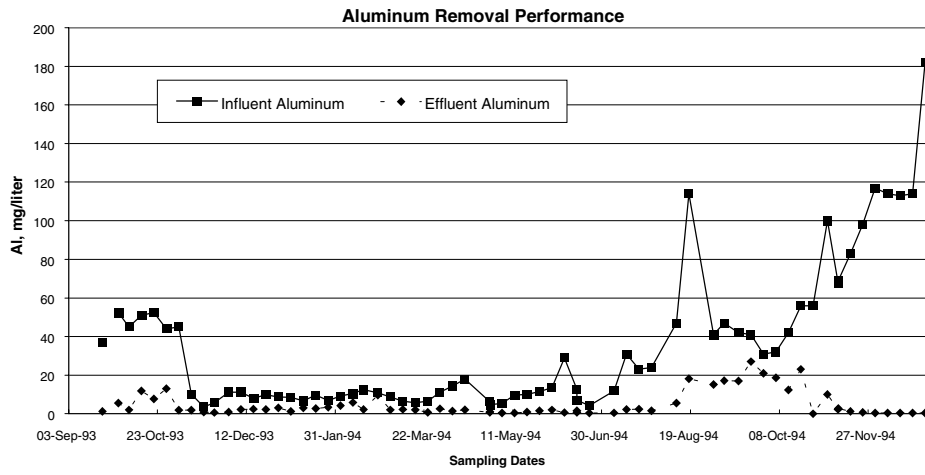


Figure 2. Brewer Pilot Passive Treatment Results.

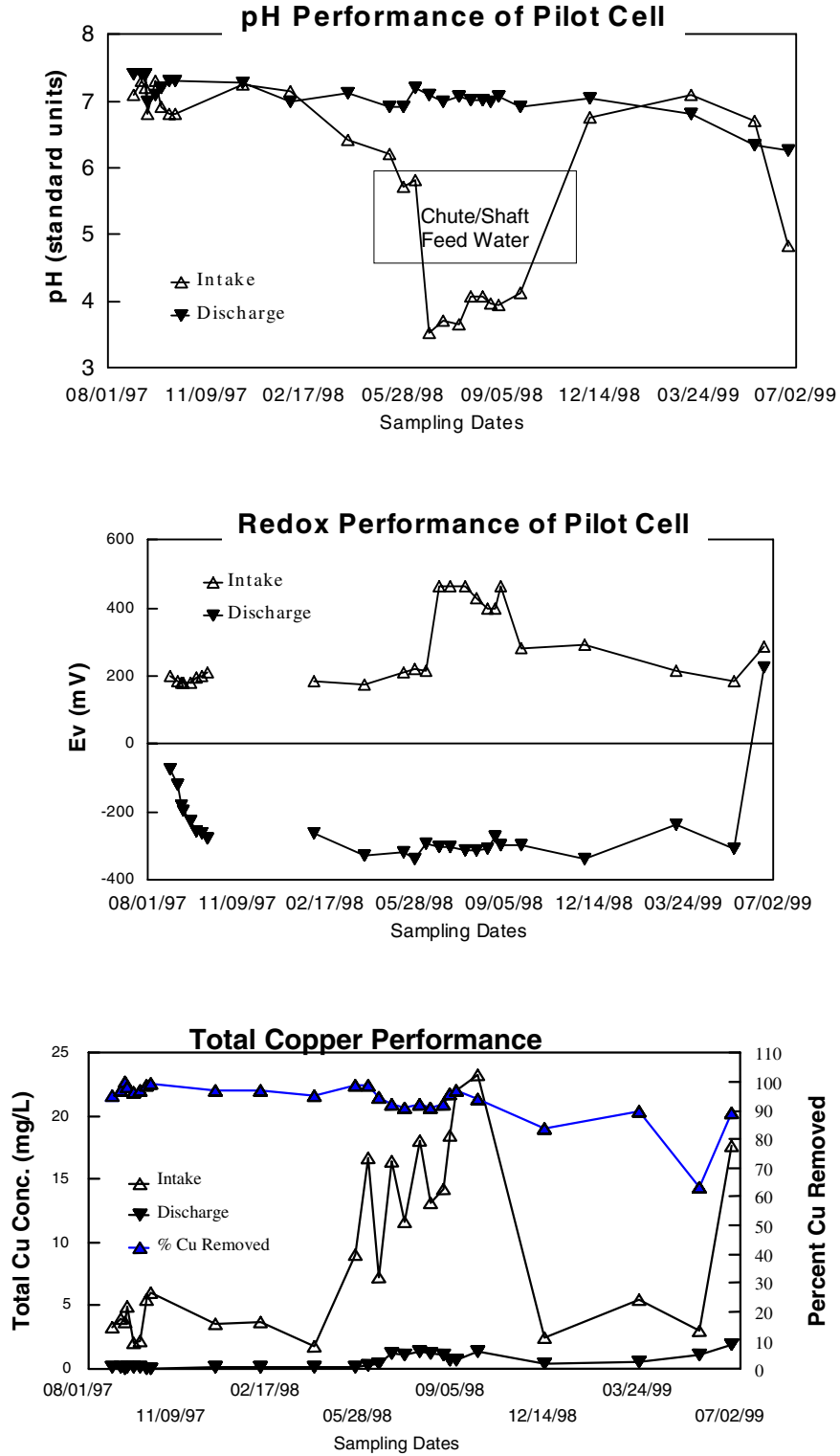


Figure 3. Ferris Haggarty Mine, WY Pilot Cell Data.

Passive Treatment of Aluminum-Bearing Acid Rock Drainage ⁽¹⁾

James J. Gusek, P.E. ⁽²⁾ , Thomas R. Wildeman, Ph.D. ⁽³⁾

Abstract: When acid rock drainage attacks clay-bearing formations at hard rock mining sites, significant amounts of dissolved aluminum can be created. The geochemistry of aluminum is complex and this can cause problems in passive treatment systems. The formation of the mineral gibbsite [Al (OH)₃] is especially problematic as it is a gelatinous solid. Gibbsite tends to form in limestone-dominated passive treatment cells and the sludge tends to plug the void spaces between the limestone rock, becoming a major maintenance problem. While the precise mechanisms have not been completely identified, the precipitation of gibbsite is avoided in sulfate reducing bacteria (SRB) cells. It is suspected that unidentified alternative aluminum compounds form in the SRB cells instead of gibbsite, and these compounds are less prone to plugging. This paper will present several case histories of SRB passive treatment projects that involved treating acid rock drainage with high aluminum concentrations.

Additional keywords: sulfate reduction, acid mine drainage, aluminosilicates, aluminosulfates.

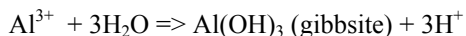
Introduction

It is ironic that many domestic drinking water treatment plants add aluminum in the form of alum as a coagulant while the mining industry works diligently to remove it from acid mine drainage/acid rock drainage (AMD/ARD). When found in a mine effluent that is actively treated using lime dosing, aluminum probably assists in the settling of iron hydroxide flocs. Conversely, the presence of aluminum in mine effluents that are passively treated typically causes maintenance headaches.

Neutralization processes that raise the pH dominate many passive treatment system components. Anoxic limestone drains (ALD's) and Successive Alkalinity Producing Systems (SAPS) are typical examples of neutralizing cell types; their ultimate goal is to add alkalinity so that iron-laden AMD/ARD is buffered against pH drops when the iron is ultimately hydrolyzed and precipitated as a hydroxide. The presence of aluminum in the AMD/ARD is problematic for SAPS and ALD's (Sterner, et al., 1997) because the geochemical conditions found in them favor the formation of the mineral gibbsite [Al (OH)₃], which is a gelatinous solid. The gibbsite sludge tends to fill the void spaces between the limestone rock used in a typical SAPS or ALD and becomes a major maintenance problem. Small amounts of aluminum in the AMD/ARD thus preclude the use of an ALD; aluminum can be tolerated in minor amounts by SAPS units, but periodic flushing of sludge from the unit (about once every several months) is required to maintain cell effectiveness.

Geochemistry of Aluminum

The dissolution of aluminosilicates such as clay minerals by the oxidizers (hydrogen ion and ferric ion) in AMD/ARD is the primary source of dissolved aluminum in typical AMD/ARD solutions. Coincidentally, it is also the source of any dissolved silica (SiO₂) or (H₄SiO₄ [aq]). The precipitation of solid-phase aluminum from AMD/ARD can be complex. The primary reaction most familiar to workers in AMD/ARD mitigation is the precipitation of gibbsite, as shown below.



This is the favored reaction when limestone dissolution or other alkalinity source abruptly raises the pH of the ARD/AMD. As previously discussed, this reaction is problematic due to sludge buildup in limestone-dominated passive treatment structures.

(1) To be presented at the 23rd Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV April 16-17, 2002.

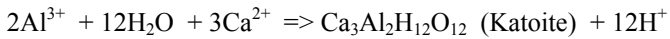
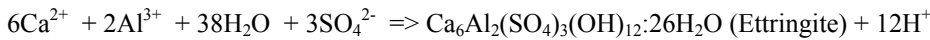
(2) James J. Gusek, P.E., is a Senior Project Manager, Knight Piésold and Co., Denver, CO 80265.

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There are many other aluminum-related reactions possible, complicated by:

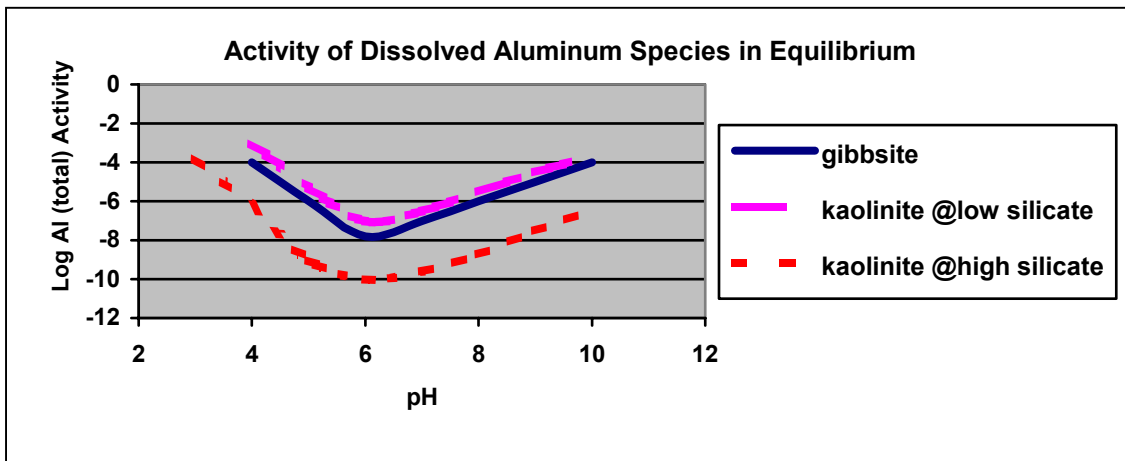
- organic matter in the form of ligands (Drever, 1988), which may tend to keep aluminum in solution through a complexation process called chelation, and
- the presence of other anions and cations.

Drever (1988) noted that the activities (or relative concentrations) of other ionic species can affect the solubility of gibbsite, particularly silica and other anions like sulfate, magnesium and potassium. The following chemical equations are offered as a sample of the over 100 potential reactions that may be possible for precipitating aluminum from the dissolved condition:



The presence of organic molecules such as humic acid, fulvic acid, formic acid or other organic and inorganic ligands have been shown to complex with aluminum and form aqueous compounds that may be mildly resistant to chemical precipitation or encourage the formation of non-gibbsite complexes (Sposito, 1996). The fluoride ion is especially notorious in creating strong ionic complexes with aluminum that are difficult to disrupt. (Drever, 1988).

To illustrate the complexity of aluminum solubility in the presence of a particular anion, the following solubility diagram for total aluminum with two dissolved silicate activities is presented. At low silicate concentrations, the formation of gibbsite is favored over kaolinite; in this instance, silicate activity was 1×10^{-5} . At a higher silicate activity (1×10^{-2}), the reverse is true and the formation of kaolinite is favored over gibbsite in the entire range of pH values. Similar trends are found in other silicate species such as pyrophyllite $[\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2]$.



Ref: After Drever, 1988

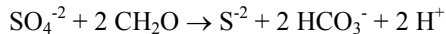
In summary, it is well established that the solubility of various aluminum species can be controlled by factors other than pH.

Sulfate Reducing Bioreactors

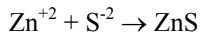
Sulfate reduction has been shown to effectively treat AMD/ARD containing dissolved heavy metals, including aluminum, in a variety of situations. The chemical reactions are facilitated by the bacteria *Desulfovibrio* in sulfate reducing bioreactors as shown in cross section below. The sulfate reducing bacterial reactions involve the generation of:

- *Sulfide ion* (S^{2-}), which combines with dissolved metals to precipitate sulfides, and
- *Bicarbonate* (HCO_3^-), which has been shown to raise the pH of the effluent.

The sulfate reducing bacteria, which appear to function best above pH 5.0, produce sulfide ion (S^{2-}) and bicarbonate (HCO_3^-) in accordance with the following reactions (Wildeman, et al., 1993):



The dissolved sulfide ion precipitates metals as sulfides, essentially reversing the reactions that occurred to produce ARD. For example, the following reaction occurs for dissolved zinc, forming amorphous zinc sulfide (ZnS):



The geochemical behavior of aluminum in sulfate reducing bioreactors has not been documented beyond preliminary evidence as discussed below in three case histories. Suspected reasons for the observed behavior are offered subsequently in the paper.

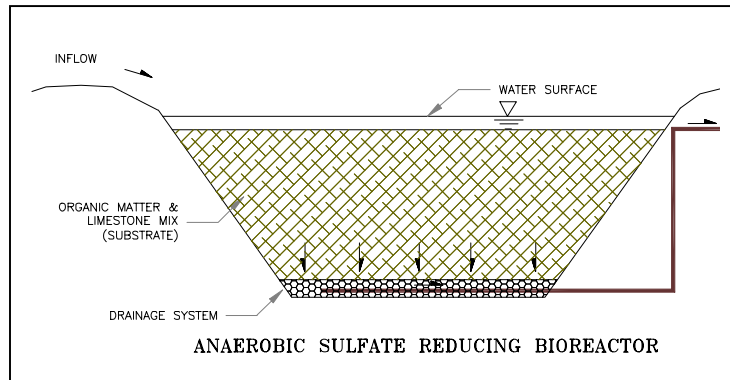
Case Histories

Knight Piésold has been involved with about two dozen AMD/ARD and mine water remediation projects, some of which have resulted in the construction of large-scale systems. Discussion of selected results from three of these sites that involved aluminum follows.

Underground Coal Mine, Pennsylvania

An underground coal mine in western Pennsylvania, closed in 1985, had mined coal from the Lower Kittanning Seam. The mine pool that developed is relatively small and its level is controlled by mine pumps that currently feed a lime dosing treatment system. The pumping rate varies with local precipitation from about 11 to over 220 gpm. The acidic drainage has a pH of about 2.8, iron of 130 mg/L, aluminum of about 30 mg/L, manganese of about 2 mg/L and acidity of 450 mg/L.

In August 2000, six bench-scale test cells were operated for 12 weeks to evaluate the application of SRB anaerobic bioreactors at the site. Bench test cell volumes were about 180 liters (32 gallons); treatment flow was about 6.5 ml/min (9.4 liters per day). The cells were filled with a mixture of chipped wood, sawdust, crushed limestone, cow manure, mushroom compost and hay in varying amounts. The results of the bench test showed similar treatment efficiencies among the test cells; typically, 99 percent of the iron and aluminum were



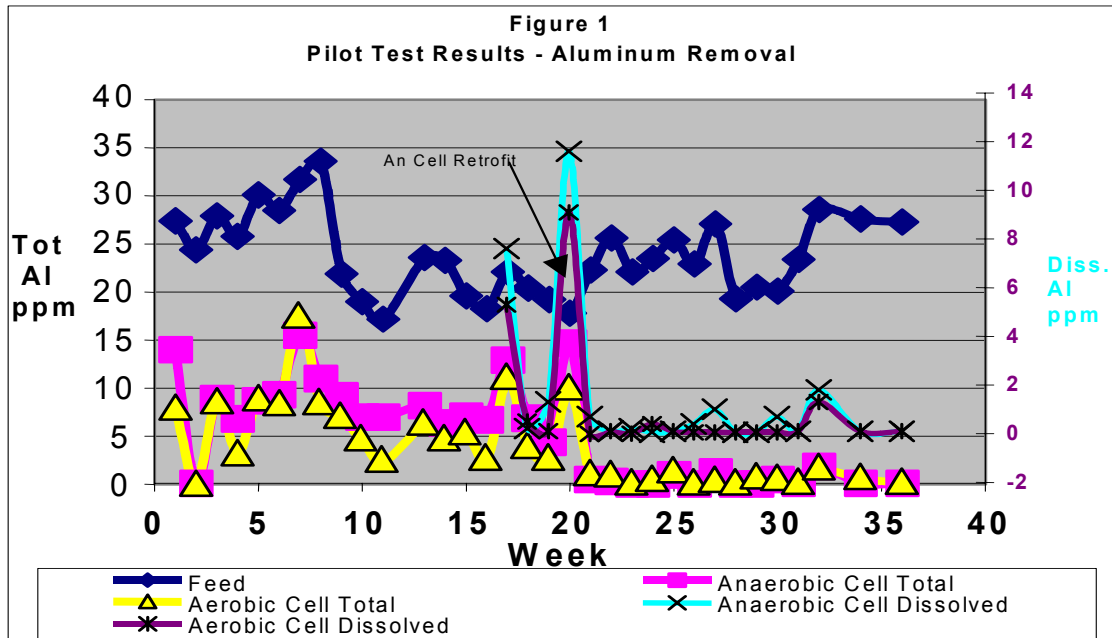
removed. Aluminum plugging was a concern, however, and one cell was sliced in half at the conclusion of the test period and no evidence of gibbsite formation was observed.

This encouraging finding supported the design of a 1.7 gpm pilot scale system (shown to the right) that was constructed in late November 2000 and operated for 14 months as of the date of this writing, March 2002. The pilot cell is about three feet deep and has a surface area of about 4,000 square feet. It feeds an aerobic polishing wetland about 120 square feet in size that discharges into a holding pond that is within the mine water management/treatment system. Data available for the first 36 weeks of operation are shown on Figure 1.



As stated earlier, the cell was commissioned in late November 2000, just as the winter season began. Incubation water temperatures were far below the ideal 10 degrees centigrade and the cell “limped” through the first 19 weeks of depressed temperature conditions. Redox and pH data suggested that conditions were favorable for sulfate reduction at anticipated design rates by Week 20. However, actual sulfate reduction rates were erratic, indicating that the cell was under stress. In early March 2001, field observations confirmed a short circuit had formed in the feed end of the cell and corrective measures were taken, which hopefully will be the topic of future paper.

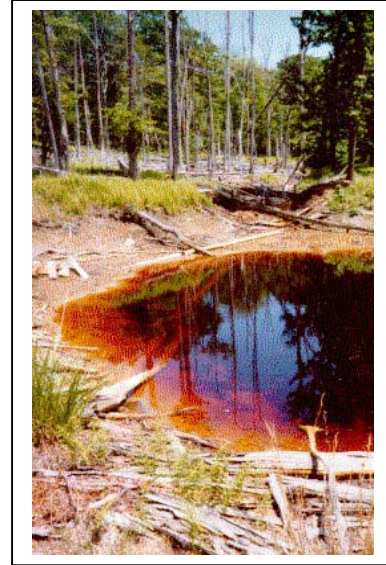
As shown on Figure 1, the aluminum removal rates improved after the retrofit and remain acceptable (less than 0.1 mg/L) despite a late-2001 increase in the feed concentration of aluminum up to 40 mg/L (Week 51) due to drought conditions.



During the operation of this SRB cell, some plugging of the effluent piping (one-inch diameter clear plastic tubing) was observed due to biological oxygen demand sludge accumulation. With the exception of the short circuiting event that required the repair, there was no other evidence of gibbsite sludge plugging during the 14 months of operation of this pilot cell.

Fran Mine, Pennsylvania

Fran Contracting mined a 37-acre surface coal mine in East Keating Township, Clinton County, Pennsylvania in Sproul State Forest. Mining of the site from 1974 to 1977 resulted in post-mining discharges of AMD that destroyed aquatic life in 2.8 miles of Camp Run, 1.3 miles of Rock Run and 2.1 miles of Cooks Run, all tributaries of the Susquehanna River. This impact occurred despite the in-situ remediation efforts that the Pennsylvania Bureau of Abandoned Mine Reclamation (BAMR) conducted in 1993. BAMR personnel have characterized the quality of discharge from this site as the “worst AMD/ARD in the entire State of Pennsylvania from a surface coal mine”. The AMD/ARD averages 2,900 mg/L of sulfate, 2,800 mg/L of acidity, 407 mg/L of iron, **237 mg/L of aluminum**, and 42 mg/L of manganese. It has a pH of about 2.3 or less and also contains heavy metals including copper, zinc, cadmium, chromium and arsenic. While the source of the AMD is a coal mine, it is comparable to AMD/ARD from an abandoned metal mine. Peak flow rate from this site is only 30 gpm, but this loading is enough to impact five miles of potential fishery downstream.

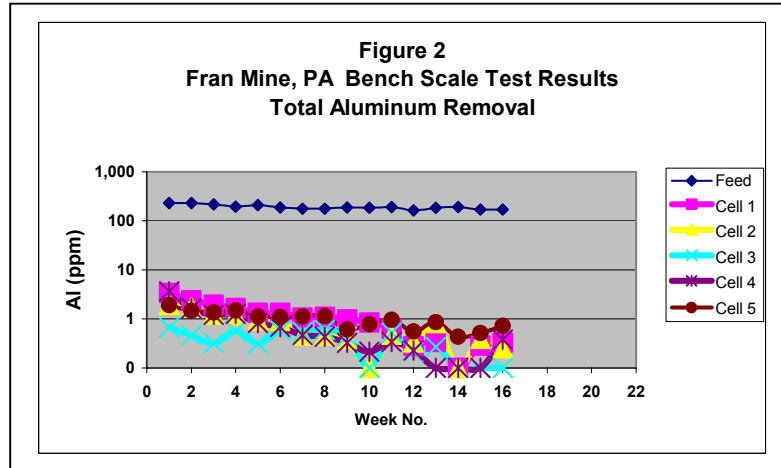


In early August 2001, Knight Piésold, supported by funding secured by the Allegheny Mountain Chapter of Trout Unlimited, constructed five bench-scale SRB bioreactors with the assistance of BAMR personnel. The five cells, built using various organic substrate mixtures, were operated for about 20 weeks. Figure 2 is a plot of the results for aluminum removal for the first 18 weeks.

Figure 2 below shows that with the exception of Cell 5, which was a cell with a high limestone content (50 percent by weight), the cells behaved similarly in removing metals and improving the pH of the Fran Mine feed water. While all the cells showed similar results, the iron removal efficiency of Cell 4 showed the best performance compared to the other four cells. In the final six weeks of sampling data, the total iron concentration in the influent to all cells averaged about 370 mg/L. Effluent from Cell 4 averaged 3.7 mg/L; Cells 1 and 2, the next best with regards to iron, averaged 20.1 and 47.5 mg/L, respectively, over the same period. Aluminum removal was excellent for all cells. The last six week average feed concentration was 178 mg/L. Effluent concentration for the cells ranged from 0.21 mg/L (Cell 4) to 0.67 mg/L (Cell 5) during this time period.

In mid-January 2002, all cells were subjected to an “autopsy” to evaluate how much, if any, plugging occurred due to the precipitation of metal sulfides and other metallic compounds during the test period. The autopsies of the cells did not reveal any visible accumulations of aluminum precipitate, even in Cell 5. The effluent pipe and limestone drainage layers were typically clean. Unfortunately, the cells were frozen, so it was not possible to closely examine the substrate for traces of aluminum deposits. Regardless, all cells operated from early August to late December without any need for “flushing” to maintain the flows.

This is encouraging from a maintenance standpoint; the full-scale sulfate reducing cells may be able to operate unattended for years, perhaps decades, without requiring flushing, major maintenance, or retrofitting. This needs to be confirmed at a pilot scale; a pilot cell is planned for construction in the spring of 2002.



Prior to the start of dissecting the bench cells, sample aliquots were recovered from the feed water holding tank, and the discharge pipes of Cells 2, 4 and 5. These samples were submitted to the Colorado School of Mines for total metals analysis using an induction coupled plasma spectrometer or ICP unit. The results of the analysis are shown on Table 1. This analysis confirms that there are other heavy metals present in the Fran Mine AMD that might impact Cook's Run, including trace amounts of cadmium, cobalt, copper, chromium nickel, and zinc. The results in Table 1 suggest that the sulfate reduction in the bench cells, especially Cell 4, was very efficient at lowering the concentration of these other heavy metals in addition to the iron and aluminum that were analyzed weekly.

Table 1
Fran Mine Bench Scale Final Samples
ICP Analysis by Colorado School of Mines Chemistry Department

Parameter	Duplicates		Bench 2	Bench 4	Duplicates		Det. Limits
	Feed Sample 1	Feed Sample 2			Bench 5A	Bench 5B	
Aluminum	382	305	0.11	BDL	0.09	0.17	0.02
Cadmium	0.12	0.10	0.01	0.00	0.03	0.03	0.00
Cobalt	2.96	2.40	0.06	0.02	0.26	0.22	0.01
Chromium	0.20	0.16	BDL	BDL	0.01	0.01	0.00
Copper	1.99	1.61	BDL	0.01	BDL	BDL	0.00
Iron	876	709.16	38.10	0.66	94.21	107.22	0.00
Manganese	97.95	79.28	21.77	2.86	38.34	38.80	0.00
Nickel	3.60	2.93	0.03	0.04	0.28	0.24	0.00
Sulfur	1,846	1,463	466	69	417	446	0.06
Sulfate (calc'd)	5,538	4,389	1,398	207	1,251	1,338	n/a
Silicon	85.22	66.96	11.36	6.83	41.70	45.67	0.01
Tin	0.22	0.17	0.04	BDL	BDL	BDL	0.02
Zinc	7.05	5.75	0.02	0.05	0.10	0.06	0.00

It is curious to note the marked decrease in silicon, from about 77 mg/L in the feed water (average of 68 and 85 mg/L) and about 7 mg/L in the Cell 4 effluent. This reduction suggests that silicate-based metal compounds, perhaps higher density aluminosilicates, might be forming in the substrate in lieu of the typical gibbsite which is so problematic in many SAPS and other limestone-based passive treatment systems.

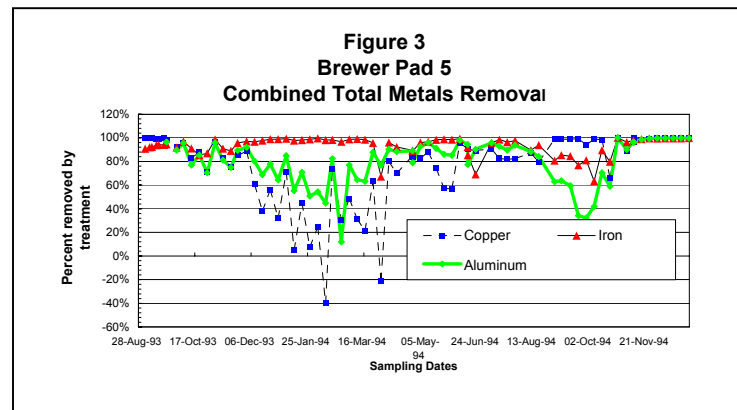
Brewer Gold Mine, South Carolina

This open pit gold mine (which has since been closed) had two AMD/ARD sites, a flooded open pit and a spent cyanide heap leach pad. Two pilot scale sulfate-reducing cells were built, one of which is shown in the photo on the right. The cells were filled with a mixture of composted turkey manure, sawdust, phosphate rock reject (limestone), and cow manure SRB inoculum. The cells treated 3.8 and 2.8 L per min (1.0 and 0.75 gpm) (pit and pad flows, respectively) for approximately 18 months. This discussion focuses on the treatment of spent heap leach pad (Pad 5) effluent. The pad had been rinsed to reduce cyanide concentrations, but its effluent had turned acidic.



This sulfate reducing cell was described in more detail elsewhere (Gusek, 2000). Throughout the testing program, Pad 5 influent concentrations fluctuated in response to rainfall events on the heap and the presumed rise of pyrite oxidation activity as buffering leach solutions were rinsed out. Iron concentration varied from 8 mg/L after a leach solution flush to about 3,950 mg/L at cell decommissioning; pH values varied from 4.7 down to 2.0 at decommissioning. Aluminum concentration in the raw feed to the Pad 5 cell averaged about 60 mg/L with a range of 4 to 220 mg/L. At the time of the pilot testing (1994-1995), there was more concern about the iron concentrations than the aluminum values.

Typical cell effluent values included a pH of 6.5, iron of 44 mg/L and aluminum of 6 mg/L. As shown in Figure 3 below, the removal of aluminum in the cell was erratic. This occurred in response to changing redox conditions that were traced to the effects of plant growth on the cell surface. Regardless, there were no indications of gibbsite formation during the 18-month pilot test.



Suspected Aluminum Behavior in Sulfate Reducing Conditions

Visual observations of organic substrates during sulfate reducing bench cell autopsies at the Fran Site failed to detect gibbsite despite being exposed to aluminum concentrations over 200 mg/L. The operation of pilot scale cells for over year at the Dixon Run No. 3 Site in Pennsylvania and the 18 month test at the Brewer Mine in South Carolina did not exhibit plugging conditions that might be attributed to gibbsite formation. It is suspected that aluminum species that are physically denser than gibbsite are being preferentially precipitated in the reduced conditions found in a typical sulfate reducing bioreactor.

Geochemical modeling may reveal likely mineral phase candidates that may be forming. These may include silicates like kaolinite or pyrophyllite or aluminum sulfates like jurbanite, diaspore, boehmite or basaluminite. Even with modeling results, however, the precise mechanisms that occur in different sulfate reducing bioreactors might be site-specific and generalizations on the phenomenon may prove to be elusive.

Mitchell and Wildeman (1996) compared the behavior of aluminum predicted by a geochemical model (MINTEQA2) with laboratory test results. Most of the mineral phases considered were either aluminum hydroxides or aluminosulfate species. They found that modeling results required some adjustments to better match their laboratory test data. In particular, it was difficult to account for all the aluminum precipitation assuming just one species; jurbanite and diaspore caused the precipitation of too much aluminum and boehmite and basaluminite caused the precipitation of too little.

The results of rudimentary stoichiometric calculations using the Fran Mine silica values presented in Table 1 suggest that there was an insufficient amount of silica present to account for all the aluminum precipitated as an aluminosilicate species. Thus, other non-silicate species such as aluminosulfates may be forming as well. Which species forms first (i.e., aluminosilicates or aluminosulfates) will be dictated by the solubility products of the respective compounds in the conditions unique to each AMD/ARD source and the local redox conditions in the sulfate reducing bioreactor.

Summary

The three case studies provide some insight into the potential for sulfate reducing bioreactors to accept and effectively treat dissolved aluminum. The mechanisms are not well understood because of the complexity of aluminum geochemistry. Future work may involve geochemical modeling and laboratory work to further understand the phenomenon. This situation should provide many future research topics. But from a practical perspective, as long as the plugging problem is solved, AMD/ARD abatement design professionals may be provided with yet another powerful tool in the passive treatment arsenal.

Acknowledgments

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Operational results of a 1,200-gpm passive bioreactor for metal mine drainage, West Fork, Missouri

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ABSTRACT: An active underground lead mine produces water having a pH of 8.0 with 0.4 to 0.6 mg/L of Pb and 0.36 mg/L of Zn. This water is pumped at the rate of 1,200 gpm (0.076 m³/s) into a five-cell, bioreactor system covering about 5 acres (2 hectares). The gravity flow system is composed of a settling basin followed by two anaerobic bioreactors arranged in parallel which discharge into a rock filter polishing cell that is followed by a final aeration polishing pond. The primary lead removal mechanism is sulfate reduction/sulfide precipitation. The discharge has met stringent in-stream water quality requirements since its commissioning in 1996. However, there have been startup and operational difficulties. The system was designed to last about 12 years, but estimates suggest a much longer life based on anticipated carbon consumption in the anaerobic cells.

1 INTRODUCTION

The West Fork Unit is an underground lead-zinc mine purchased by the Doe Run Company from Asarco in 1998 that discharges water from mine drainage to the West Fork of the Black River (West Fork) under an existing NPDES permit. The West Fork Unit is located in Reynolds County in central Missouri, in the New Missouri Lead Belt, about three hours from St. Louis.

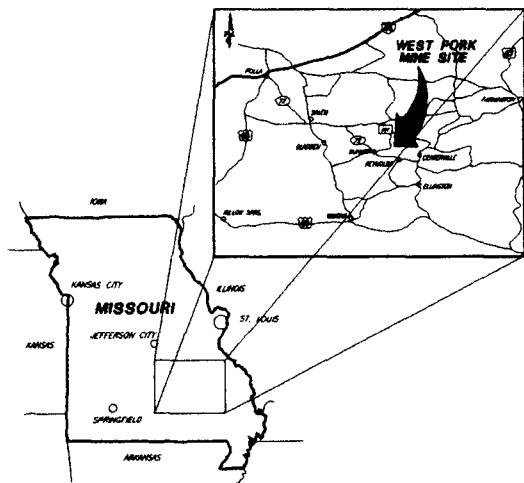


Figure 1 - Site Location

Flow rates in West Fork vary from about 20 cubic feet per second (cfs) to more than 40 cfs (0.56 to 1.13 m³/s). Water quality is relatively good, despite being located in an area with naturally high background levels of lead due to the bedrock geology. The mine discharges about 1,200 gpm (2.7 cfs or 0.076 m³/s) on the average or about 10 percent of the total flow in West Fork.

The adoption of water quality-based discharge limits, in its NPDES permit issued in October 1991, prompted Asarco to evaluate treatment methods for metal removal. Evaluations of alternative treatment processes determined that biotreatment methods were feasible and cost less than half as much as active sulfide precipitation. The goal of the water treatment project was to ensure that the stringent water quality-based limits in the permit would be consistently met.

Since 1987, a group from Knight Piésold and Co. and the Colorado School of Mines has been active in developing passive treatment methods for metal-mine drainages. The primary treatment method is through the generation of hydroxides and sulfides through microbial metabolism. The biogeochemical principles are summarized in Wildeman, et al. (1995), and Wildeman and Updegraff (1998). The design principles are explained in Wildeman, Brodie, and Gusek (1993). In the case of the West Fork Unit, biotreatment consists of two stages:

1. An anaerobic unit that generates sulfide through sulfate reduction and is responsible for the lead removal.
2. An aerobic unit that is a rock filter/wetland. This unit is responsible for removing dissolved organic matter and excess sulfide from the effluent from the anaerobic cell. The aerobic unit also reoxygenates and polishes the water before it enters the river.

Extensive laboratory, bench-scale, and pilot scale tests were made on the anaerobic unit. These are described in Wildeman, et al. (1997), and Gusek, et al. (1998). The design and permitting of the system are also discussed in Gusek, et al. (1998), and Wildeman, et al. (1999). This paper concentrates on the operation of the full-scale system since its start in 1996.

2 SYSTEM DESCRIPTION

The system was designed based on the performance of the pilot-scale reactor and the interim bench scale studies. The large-scale system was estimated to cost approximately \$500,000 and required about three months of construction time. Operational costs include water quality monitoring as mandated by law. No additional costs for reagents are incurred; since the system uses gravity flow, moving parts are few and include valves, minor flow controls, and monitoring devices. Based on carbon depletion rates observed in the pilot system, the anaerobic cell substrate life was projected to be greater than 30 years; the full-scale biotreatment system should be virtually maintenance-free. Should mine water quality deteriorate, the full-scale design included a 50-percent safety factor.

The biotreatment system is composed of five major parts: a settling pond, two anaerobic cells, a rock filter, and an aeration pond (Knight Piésold, 1997). The system is fully lined. The design was also integrated into the mine's pre-existing fluid management system.

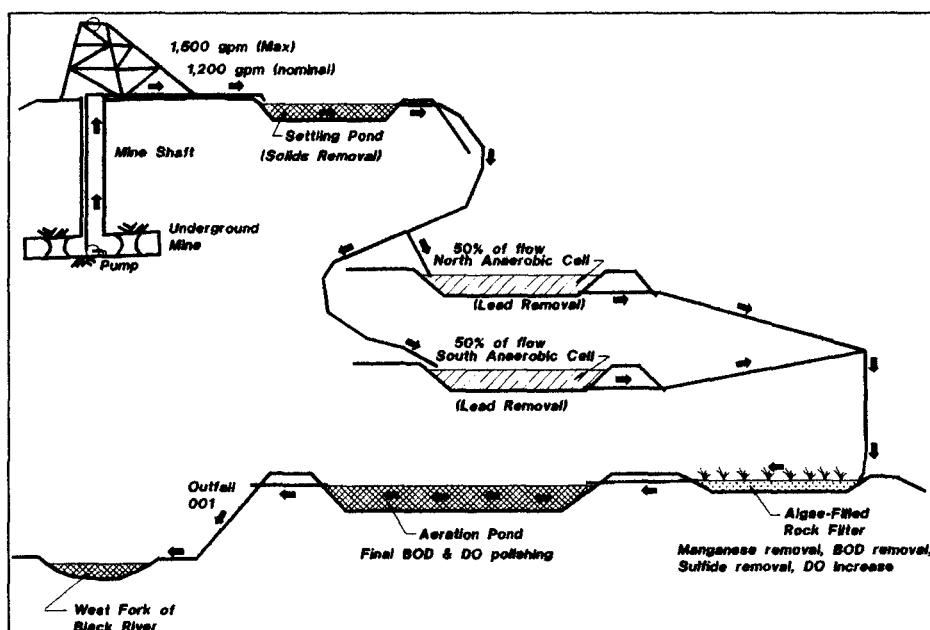


Figure 2 - System Configuration

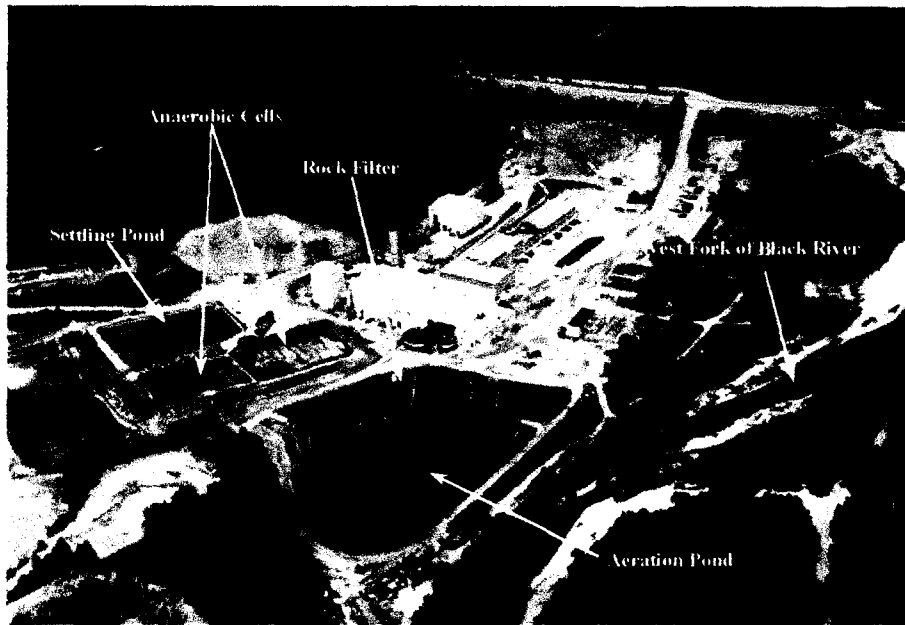


Figure 3 - Aerial View

A rectangular-shaped, 40-mil HDPE-lined settling pond has a top surface area of 32,626 ft² (3,030 m²) and a bottom surface area of 20,762 ft² (1,930 m²). The sides have slopes of 2 horizontal to 1 vertical (2H:1V). The settling pond is nominally 9.8 ft (3 m) deep. It discharges through valves and parshall flumes into the two anaerobic cells.

Two anaerobic cells are used, each with a total bottom area of about 14,935 ft² (1,390 m²) and a top area of about 20,600 ft² (1,930 m²). Each cell is lined with 40-mil HDPE and was fitted with four sets of fluid distribution pipes and three sets of fluid collection pipes, which were subsequently modified (see Start Up discussion). The distribution/collection pipes were connected to commonly shared layers of perforated HDPE pipe and geonet materials sandwiched between layers of geofabric. This feature of the design was intended to allow control of sulfide production in hot weather by decreasing the retention time in the cell through intentional short circuiting.

The spaces between the fluid distribution layers were filled with a mixture of composted cow manure, sawdust, inert limestone, and alfalfa, referred to hereafter as “substrate.” The total thickness of substrate, piping, geonet, and geofabric was about 6 feet (2 m). The surface of the anaerobic cells was covered with a layer of crushed limestone. Water treated in the anaerobic cells flows by gravity to a compartmentalized concrete mixing vault and thereafter to a rock filter cell. The gravity-driven flows can be directed upward or downward.

The rock filter is an internally bermed, clay-lined shallow cell with a bottom area of about 63,000 ft² (5,900 m²) and a nominal depth of one foot (30 cm). It is constructed on compacted fill that was systematically placed on the west side of a pre-existing mine water settling pond. Limestone cobbles line the bottom of the cell, and the cell is compartmentalized by limestone cobble berms. The discharge from the rock filter flows through a drop pipe spillway and buried pipe into a 40-mil HDPE-lined aeration pond. The aeration pond surface covers approximately 85,920 ft² (8,000 m²). The aeration pond discharges through twin 12-inch (30-cm) HDPE pipes into a short channel that leads to monitoring outfall 001 and thence into West Fork.

After the water pumped from the underground mine enters the settling pond, all flows are by gravity.

3 START-UP EXPERIENCE

Bench-scale test results suggested that the anaerobic cells be incubated with settled mine water for about 36 hours or less before fresh mine water was introduced at full flow to minimize initial levels of BOD, fecal coliform, color, and manganese. For about two weeks, pumps recycled the water within the two anaerobic cells. Based on data collected in field, and subsequent laboratory confirmation, the water from the anaerobic cells was routed to the tailings pond for temporary storage and later treatment and release. At that point, the rock filter and aeration ponds were brought on-line. In the meantime, the mine discharged according to plan through an overflow pipe from the settling pond as it had during construction of the other components.

After about six weeks of full-scale operation, the apparent permeability of the substrate was found to be lower than expected and the system was operating nearly at capacity. The system had been designed so that either of the two anaerobic cells could accept the full flow amount on a temporary basis in case maintenance work required a complete cell shutdown.

Research found that H₂S gas, generated by the sulfate-reducing bacteria, was being retained in the substrate in the anaerobic cells; this created a gas-lock situation that prevented full design flow. A temporary solution was obtained by periodic "burping" of the cells using the control valves. However, the "burping" had to be performed at 24-hour intervals, and it was determined that this solution was too labor-intensive.

The sulfide gas lock problem was investigated in December 1996 by installing vent wells in the substrate and measuring the gas pressures. Observations indicated that the gas was a factor in apparent short circuiting of the water passing through the cell. The layered geotextiles (geonet and geofabric), originally intended to promote horizontal flow, appeared to be trapping the sulfide gas beneath them and vertical flow was being restricted. The permeability of the substrate itself was for the most part unaffected. However, construction practices in the south anaerobic cell could have contributed to the situation. Here, a low ground bearing bulldozer was used to place substrate in nominal 6-inch (15-cm) lifts. This could have created a layering effect that may have trapped gas as well. Substrate layers in the north anaerobic cell were placed in a single lift, and no layering effect was observed during subsequent excavation. It is noteworthy that the mid-cell geotextiles had not been a feature of the pilot test cell design.

The first phase of a permanent solution was implemented with a trenching machine that ripped through the geonet/geofabric layers in the south anaerobic cell. This disrupted the gas-trapping situation. Subsequently, the substrate from the entire south anaerobic cell was excavated and the cell refilled without the geotextiles in June 1997. Identical action was taken on the north anaerobic cell in September 1997. These actions have solved the gas lock problem.

4 MAINTENANCE EXPERIENCE

Although this is technically a passive treatment system, when one considers trying to direct the flow of 1,200 gpm (0.076 m³/s) through approximately 3,930 yd³ (3,000 m³) of material there is certain to be some hydraulic problems. In addition, the design of the anaerobic cells made provisions for the water to bypass portions of the cells during the summer to eliminate excess buildup of sulfide in the cell effluent. In the summer of 1997 and 1998, operation of the system included by-passing some portions of the cell to maintain lower sulfide concentrations. However, when this was tried, short-circuiting within the cells and plugging of the substrate made maintenance during the summer more extensive than during the winter.

Perhaps the most troublesome maintenance issue was that a combination of sediment in the mine water along with algae buildup on the cell surfaces would block the infiltration of water into the cells.

This would necessitate periodically draining the cells and rototilling the top of the substrate so as to break up the accumulation cake. Often at the same time as a cell was tilled, water would be back-flushed through the discharge pipes to dislodge precipitate accumulation. When such maintenance was done, the rock filter would still receive discharge. It has proved to be an effective buffer between the cells and the discharge pond. This maintenance cycle of tilling and back-flushing had to be done almost once a month during the summer of 1998. During the winter, buildup was not as extensive and maintenance of the cell surfaces was less frequent. Currently, schemes are being investigated to try a drastic reconditioning of the cells to permanently increase the hydraulic conductivity of the anaerobic cells.

Other than repairing a bubble that appeared under the liner of the aeration pond, there has been no maintenance needed on the rock filter and the aeration pond.

5 OPERATIONAL RESULTS

5.1 The Anaerobic Cells

The average influent water quality can be compared with discharge water quality (Table 1) during the June through November 1997 period. Discharge levels of Pb and other metals were reduced substantially from average influent levels. For Pb, the level was reduced from a typical average of 0.40 mg/L to between 0.027 and 0.050 mg/L. Zn, Cd, and Cu effluent concentrations were also reduced.

Table 1 - West Fork Mine Water Quality Data

Parameter	Typical Average Influent Water Quality in mg/L	Range of Water Quality Discharge in mg/L (June - November 1997)
Pb	0.4	0.027 - 0.050
Zn	0.36	0.055 - 0.088
Cd	0.003	<0.002
Cu	0.037	<0.008
Oil and Grease	--	<5.0
H ₂ S	--	0.011 - 0.025
Total Phosphorus	--	<0.05 - 0.058
Ammonia as N	0.52	<0.050 - 0.37
Nitrate and Nitrite	2	<0.050 - 1.7
True Color	--	10 - 15
BOD	1.7	<1 - 3
Fecal Coliform	—	<1 - 2
pH	7.94	6.63 - 7.77
TSS	—	<1 - 4.2

More extensive analysis of the operational data from June 1997 through June 1999 has shown some interesting results. The plumbing system in the anaerobic cells was designed to run the cells upflow or downflow, to use a portion of the cell when sulfide production became too high, and to be back-flushed in case precipitation occurred in the discharge line. All three features have been used. The cells have been run in the upflow direction during the first winter so that the substrate compaction that occurred during the summer could be relieved. The three levels of discharge pipes are routinely monitored for

sulfide production, and the valves are adjusted accordingly to eliminate excess sulfide. In the summer, these adjustments become more difficult as attempts are made to only use portions of the cells. In addition, the cells are routinely back-flushed to maintain good circulation of mine water through the cells.

By operating the anaerobic cells in this fashion, over four seasons from July 1997 to July 1998, the average concentration of 40 analyses of total Pb in the water entering the cells is 0.45 and the average concentration of Pb in the water exiting the cells is 0.085. Results for zinc are not as extensive. From March 1998 to November 1998, the average concentration of 10 analyses of total Zn in the water entering the cells is 0.44 and the average concentration of Zn in the water exiting the cells is 0.102.

Within the anaerobic cells, production of enough sulfide has never been a problem. During the summers of 1997 and 1998, sulfide concentration in discharges from some portions of the cells routinely exceeded 12.0 mg/L, the upper quantitation limit of the analytical procedure. This correlates with the pilot cell results where, during the two summers in which it operated, sulfide concentrations reached 20 mg/L. According to Wildeman, et al. (1997), at this level of sulfide concentration, the production of sulfide in the anaerobic cells is about 2 moles sulfide per cubic meter per day. As expected, during the winter, concentrations of sulfide in the cell effluent are lower. However, even during the months of December, January, and February, sulfide concentrations in the discharge from some portions of the cell were between 2.0 and 7.7 mg/L. These concentrations have been higher than the average of 0.3 mg/L of sulfide that was found during the winter the pilot cell operated (Wildeman, et al., 1997).

5.2 The Rock Filter

Of the five parts of the system, the operation of the rock filter has been the most interesting. It operates as a natural wetland where water of a depth of 1 to 2 feet (30 to 60 cm) meanders through the limestone cobbles. Flora and fauna have thrived in this ecosystem. It has served the important function of cleansing the excess sulfide in the water that is leaving the anaerobic cells. From July 1997 to September 1998, the average of 55 analyses of sulfide concentration in the water entering the rock filter is 3.3 mg/L. In 55 analyses of sulfide in the rock filter effluent, sulfide was detected in the water 20 times and none of these were above 0.25 mg/L.

Because the water entering the rock filter contains a significant concentration of sulfide, a unique ecosystem of algae and bacteria have developed in this area. In the summer of 1997, red algae/bacteria started to develop in this influent area and have persisted. In addition, a white scum has developed in this area. Indeed, the rock-filter influent area looks like a pool of the primordial soup. During the summer of 1997, when high levels of sulfide were entering the rock filter, the water would develop a milky white colloidal suspension that would persist throughout the wetland system. This milky suspension had diurnal characteristics. It would be more persistent in the morning and sometimes clear up during the day. In the summer of 1998, this milky suspension was not as evident even though the concentrations of sulfide entering the rock filter were sometimes higher. Vegetation in the rock filter was much more lush in the second summer. The speculation is that this milky suspension is colloidal sulfur. If it is, then this form of wetland ecosystem removes it.

Besides removing sulfide from the water, the rock filter also plays a significant role in further reducing the concentration of lead in the water. Over four seasons from July 1997 to July 1998, the average concentration of 40 analyses of total Pb in the water entering the rock filter is 0.085 and the average concentration of Pb in the water exiting the rock filter is 0.050. The mechanism for lead removal in the rock filter is not known.

6 CONCLUSIONS

In the introduction to this paper it was stated that the biotreatment system should be virtually maintenance free. That has not been the case with the anaerobic cells. Keeping these cells from clogging has required periodic rototilling and back-flushing. Because attempts were made during the summer to use only a portion of the two cells, maintenance has been more extensive at this time than during the winter. Nevertheless, these cells have performed according to design and have been effective at removing lead from the mine water. Because of this necessary maintenance, the design of the plumbing system to include back-flushing, upflow and downflow, and use of only a portion of the cell has been particularly advantageous.

The need for the rock filter has been found to be essential. Its operation has shown some surprises. The presence of sulfide in the water has caused a unique ecosystem that effectively removes this constituent from the water. The removal of sulfide is more important in the summer. The rock filter also removes a significant amount of lead. The removal mechanism is unknown.

7 ACKNOWLEDGMENTS

The foresight and subsequent commitment of ASARCO and the Doe Run Co. to this type of treatment is most appreciated.

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Appendix E
Liquid-Reactant SRB Bioreactors

Papers by Tim Tsukamoto et al.

Sustainable Bioreactors for Treatment of Acid Mine Drainage at the Leviathan Mine

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The use of sulfate-reducing bioreactors to treat acid mine drainage has advantages over traditional treatment methods due to their semi-passive nature and low cost. These systems utilize sulfate-reducing bacteria in a flow-through design to reduce sulfate to sulfide and precipitate metals as metal-sulfides. A variety of organic substrates such as manure and wood chips have been utilized as a food source and matrix for bacterial growth. The effectiveness of these systems decreases as easily accessible reducing equivalents are consumed in the substrate through microbial activity. This results in a temporary system in which the substrate/matrix needs to be periodically replaced. We have developed a system at the Leviathan Mine, Alpine County, CA, that largely eliminates these problems by utilizing a matrix with large pore spaces in conjunction with an alcohol feed and sodium hydroxide sufficient to allow the bacteria to thrive. The large pore spaces allow flushing of the matrix to remove metal sulfide precipitates and biomass, and maintain hydraulic conductivity. Because alcohol does not freeze, use of this substrate allows us to supply the bacteria year round with a sufficient quantity of reducing equivalents to remove a specific quantity of sulfate, and in turn remove the metals from solution. Once acclimated and functioning properly with base addition, the bioreactor treatment system at the Leviathan Mine was successful at treating flows of 36 L/min. This system has now successfully treated effluent for over six months and is removing from solution approximately 600 mg/L of sulfate (40%), 100 mg/L of iron (99%), 0.6 mg/L of nickel (99%), 1 mg/L of copper (99%), 1.6 mg/L of zinc (99%) and 25 mg/L of aluminum, TDS was lowered from 2200 to 1500. Alkalinity was increased to 300 mg/L CaCO₃.

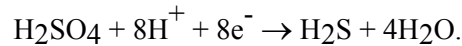
Key words: Bioreactors, wetlands, acid mine drainage, acid rock drainage, and sulfate reduction, sulfate reducing bacteria, water treatment, and mining, passive treatment systems

Introduction

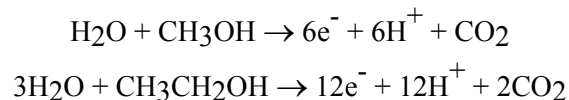
In recent years, bioreactors have been constructed and utilized for the treatment of acid mine drainage (AMD). These reactors utilize sulfate-reducing bacteria to reduce sulfate to sulfide (Tuttle et al, 1969; Wakao et al, 1979; Wildmann et al, 1990). The sulfide that is generated can subsequently precipitate metals as metal sulfides (Miller, 1950; Eger, 1994).

A simple passive to semi-passive flow-through design is generally utilized. AMD is gravity fed into a pond or tank that contains an organic substrate such as manure or wood chips. The AMD flows through the substrate where the treatment occurs and is released as water containing lower concentrations of metals with elevated alkalinity and pH. The substrate acts as a physical framework for metal sulfide precipitation and microbial attachment. In addition, the substrate serves as a carbon source for growth and maintenance of sulfate-reducing bacteria. These reactors are promising as a less expensive, passive alternative to active treatment (lime precipitation). However, the lifetime of such a reactor is limited by the amount of carbon source readily available to sulfate-reducing bacteria. Once the source of carbon is exhausted from the substrate, sulfate-reducing bacteria will no longer efficiently reduce sulfate to sulfide and treatment efficiency decreases (Tsukamoto and Miller 1999). In addition substrates such as manure plug as the manure is degraded and metals are precipitated within the substrate.

The limitations of bioreactors that utilize a substrate that serves both as a physical framework, as well as the sole source of carbon have, led to studies where the carbon source is delivered to the bioreactor continuously. Previously, we reported on the use of methanol as a carbon source added to the bioreactor influent acid mine drainage (Tsukamoto and Miller, 1999). This type of system has the advantage of longevity, as well as allowing removal of specific concentrations of sulfate and metals based on stoichiometric addition of the carbon source. For example, the reduction of sulfate to sulfide requires 8 electrons:



Methanol and ethanol contribute 6 and 12 electrons, respectively, per molecule oxidized to carbon dioxide.



Electron accounting in this manner allows determination of the number of moles of carbon source needed to reduce one mole of sulfate, and can allow appropriate titrating of alcohol for the treatment needed. Lactate (El Bayoumy et al. 1998) and ethanol (Barnes et al. 1992) have similarly been added as a continuous source of carbon. Sulfate-reducing bacteria are also known to utilize a variety of electron donors including alcohols, hydrogen, carboxylic acids, amino acids, sugars and long chain saturated alkanes (Widdel and Bak, 1992; White, 1995).

In addition, when a liquid substrate is fed to the system as a carbon source, a matrix can be utilized which contains large pore spaces. This will increase hydraulic conductivity and reduce or eliminate plugging, particularly when a flushing mechanism is incorporated into the matrix.

This work focuses on the use of ethanol, methanol and ethylene-glycol as carbon sources in a bioreactor treatment system at the Leviathan Mine. Ethanol and methanol were added as carbon sources due to their physical properties (maintained as a liquid under environmental

temperatures and can be added incrementally). This bioreactor treatment system consists of two reactor ponds containing mainly wood chips and non-reactive cobbles, and a filtration system to remove precipitated metals.

Materials and Methods

The treatment system was designed as a dual cell treatment system. Cell 1 is approximately 2m deep x 7.3m wide x 17.3 m long, with a volume of approximately 175 m³. Cell 2 is approximately 2m deep x 10.7m wide x 17.3 m long, with a volume of approximately 292 m³. AMD can be distributed to cell 1 and cell 2 in parallel or in series, at any flow rate up to the total flow of the seep (approximately 30-60 L/min). AMD enters each cell from the surface and flows laterally through the cells where it is collected in 3 loops of perforated PVC pipe located at the bottom. Inflow and outflow was originally controlled with valves. Frequent plugging of these valves forced the addition of standpipes to control flow in the effluent and a weir was constructed to control influent flow.

Both cells were lined with 40 mil PVC that was covered with approximately 0.3m of manure. The remainder of the substrate in cell 1 consisted of wood chips. Methanol was added as the source of reducing equivalents up to day 245 and a mixture of ethanol, methanol and ethylene glycol were added for the rest of the experimental period. The remainder of the substrate in cell 2 consisted of 6 to 20 cm cobble. Both cells were inoculated with an anaerobic horse manure culture upon filling the cells. Flows were maintained below 3L/min (total) up to day 237. At this time, the weir and standpipes were assembled and the flows were incrementally increased. Cells were run in series (i.e. the flow leaving Cell 1 entered Cell 2) and additional AMD was added to cell 2. Alcohol concentrations varied, but influent typically contained reducing equivalents to remove 1-3 times the amount of sulfate in solution.

Basic solutions were also added to the influent (to raise the pH for microbial growth) and effluent (for iron sulfide precipitation) following day 541 of the experiment. Influent solutions were typically increased to pH=3.8-4.3, effluent solutions were increased to pH 6.0-7.5. Following the addition of base we were able to increase flows dramatically while maintaining treatment.

Results

Problematic trace metals (Ni, Cu, Zn) and iron and sulfate were effectively removed throughout the treatment period of 1200 days. Copper was removed from an average influent concentration of 0.82 mg/L to an average effluent concentration of 0.02 mg/L. Nickel was removed from an average influent concentration of 0.41 mg/L to an average effluent concentration of 0.07 mg/L. Zinc was removed from an average influent concentration of 1.82 mg/L to an average effluent concentration of 0.09 mg/L. Iron was removed from an average influent concentration of 167 mg/L to an average effluent concentration of 3.75 mg/L. Sulfate was removed from an average influent concentration of 1750 mg/L to an average effluent concentration of 1170 mg/L.

Following, the addition of base (day 541) flows were increased from an average flow of 1.6 L/min to 24.2 L/min. The entire flow of the seep was treated the majority of the time following base addition. Metals removal was maintained following base addition, while sulfate

removal decreased only slightly despite shorter residence times within the reactor cells. Iron removal was dependant upon the effluent pH. When the effluent pH was maintained above 7.0 iron was typically removed to below 5.0 mg/L.

Discussion

Ethanol, methanol and ethylene glycol were utilized as carbon sources for sulfate-reducing bacteria in a full scale bioreactor treatment system. Treatment was maintained at low temperature and low pH. However, some base had to be added which allowed us to increase flows through the bioreactors while maintaining treatment.

Bioreactors that are designed with a carbon source that can be delivered incrementally offer distinct advantages over those with which the carbon source is contained in the substrate. They offer a means of delivering the carbon source to the reactor in stoichiometric concentrations, to remove specific concentrations of sulfate and in turn specific concentrations of divalent metals. There is little waste of the carbon source once the system is acclimated and alcohol is quantitatively removed.

These systems also offer the advantage of longevity. We have shown with previous work that carbon source availability is limited in sole carbon source substrate bioreactors and thus lifetimes are generally limited to months to a few years (Tsukamoto and Miller, 1999) depending on the characteristics of the bioreactor and influent AMD.

Finally, alcohol based bioreactors allow flexibility in the physical substrate that can be utilized within the cell. Plugging of the substrate is a common problem in substrate-limited bioreactors, especially when the substrate consists of material with small pore spaces and low hydraulic conductivity such as manure. Systems that utilize a matrix with large pore spaces can be flushed to remove metal sulfide precipitates and extend the lifetimes of the reactor.

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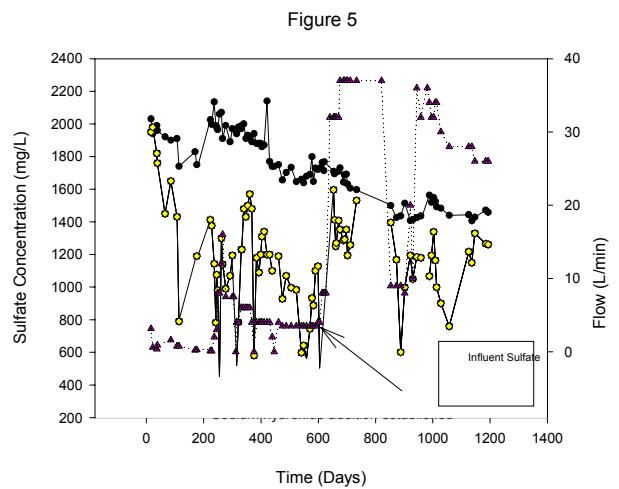
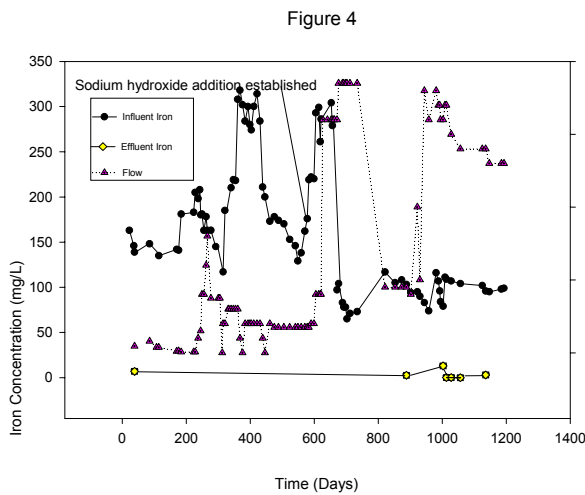
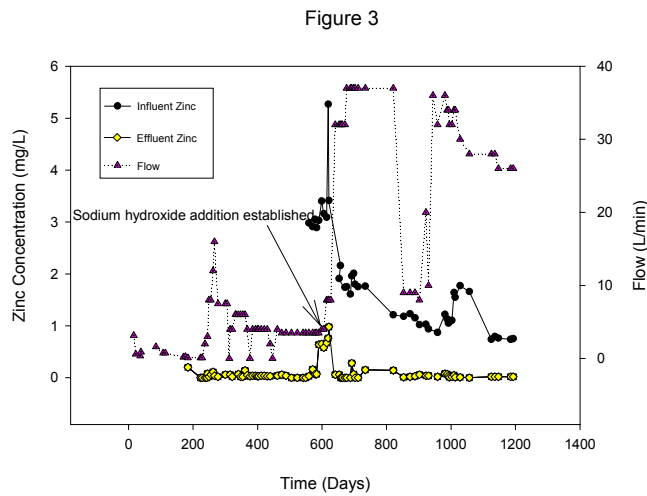
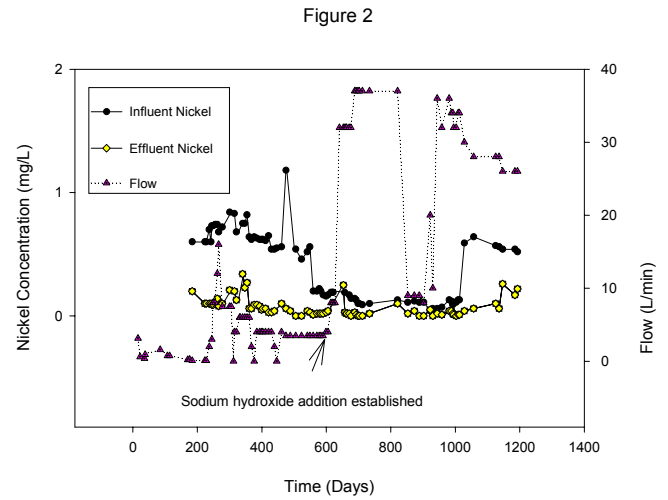
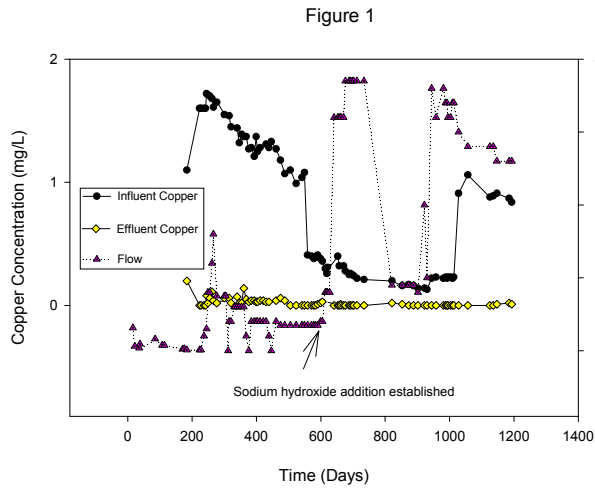
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Figures 1-5. Influent and effluent copper, nickel, zinc, iron and sulfate respectively, with flow, plotted vs time.



Sizing Alcohol Enhanced Bioreactors

The size necessary for effective metals removal in an alcohol enhanced SRB bioreactor can be determined by examining four interrelated factors. These factors are: (1) sulfate loading; (2) metal loading, (3) the residence time required for sulfate-reduction to occur and (4) the acidity of the water. The residence time must be sufficient within the bioreactor to reduce a specific concentration of sulfate and, in turn, precipitate the metals of concern.

Sulfate loading. The rate of sulfate reduction in an alcohol-enhanced bioreactor is typically faster when compared to a traditional bioreactor where the matrix is also the source of energy for the bacteria. Rates as high as 0.96 mol sulfate/(m³*day) have been observed in a methanol enhanced manure matrix reactor and rates as high as 0.56 mol sulfate/(m³*day) have been observed in a porous ethanol enhanced reactor. The differences in these rates are most likely due to additional surface area available in the manure matrix. A conservative estimate can be calculated given these rates of sulfate reduction and by determining the amount sulfate reduction required to remove the metals of concern.

Metal loading. The stoichiometric introduction of metals, including iron, copper, lead, zinc, nickel and cadmium, into the system must be less than the rate of sulfate reduction. This rate can be estimated simply by determining the metal concentrations and summing the molar concentration of metals in solution susceptible to sulfide precipitation. It is best to have a 30-100% excess of sulfate removal compared to metal concentration.

Residence time. The residence time needed in the bioreactor is based on the amount of sulfate-reduction that must occur to remove the metals of concern. The implementation of settling ponds for sludge removal adds additional residence time to the system for metal sulfide precipitation to occur.

Water Acidity. Acidity is consumed during sulfate reduction with the generation of byproducts (i.e. HCO₃⁻ and HS⁻). Therefore, the amount of sulfate-reduction needed may be determined by the amount of acidity present in the water. There are certain instances

where the acidity of the water is in excess of the amount of alkalinity generation that can be realistically obtained from sulfate reduction alone. In these instances an outside source of alkalinity may need to be added to remove residual dissolved metals.

Additional Factors. Large flow variations can overwhelm anaerobic bioreactors if they are sized for an average flow. If the flow and/or acidity and redox flux to the bioreactor increases significantly above the design, bacterial activity will decrease. In such cases, flow should be decreased significantly and the microbial activity allowed to become re-established.

In most instances the fluctuations in flow are small enough that bioreactor can handle the changes, given enough alcohol and residence time is available. However, extreme fluctuations in flow may require the implementation of a holding pond upstream from the bioreactor to regulate flow to the bioreactor at a constant rate. The temperature can also affect the rate of sulfate-reduction. However, the rate of reduced sulfate reduction is generally decreased by a small percentage and does not affect treatment if sized accordingly and the majority of the treatment area remains thawed.

Ethanol Enhanced, Sustainable Sulfate-Reducing Bioreactors

The State of the Art in Passive Treatment Systems
Draft

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TKT Consulting, LLC

Prepared for: URS

October 23, 2002

Introduction

In recent years, bioreactors have been constructed and utilized for the treatment of acid rock drainage (ARD). These reactors utilize sulfate-reducing bacteria to reduce sulfate to sulfide (Tuttle et al, 1969; Wakao et al, 1979; Wildmann et al, 1990). The sulfide that is generated can subsequently precipitate metals as metal sulfides (Miller, 1950; Eger, 1994).

Treatment of ARD in the past has usually involved active processes such as lime precipitation (Perry and Kleinmann, 1991). During the lime precipitation process the ARD is neutralized by the addition of lime, and metals are subsequently removed as oxide and hydroxide precipitates (Perry and Kleinmann, 1991; Watzlaf, 1998). Although these processes are usually effective at removing contaminants, they produce large amounts of sludge of primarily gypsum, and are expensive and labor intensive (Perry and Kleinmann, 1991). Bioreactors have advantages over lime treatment, particularly for flows of less than 200 gallons/min and moderate acidity. The process of contaminant removal is accomplished by reversing the chemistry of acid generation. Metals and sulfate are reduced and removed as metal sulfides. The solubility product constants for metal precipitates commonly used in ARD treatment are listed in the following table.

Table 1. Solubility Product Constants for Metal Precipitates (Data from CRC Handbook of Chemistry and Physics 1985)

Substance	Solubility Products		Substance	Solubility Products		Substance	Solubility Products
Bi ₂ S ₃	1.8 x 10 ⁻⁹⁹		CoS	9.7 x 10 ⁻²¹		Mn(OH) ₂	2.04 x 10 ⁻¹³
HgS	6.38 x 10 ⁻⁵³		NiS	1.08 x 10 ⁻²¹		MnS	4.55 x 10 ⁻¹⁴
Ag ₂ S	6.62 x 10 ⁻⁵⁰		Pb(OH) ₂	1.4 x 10 ⁻²⁰		PbCO ₃	1.48 x 10 ⁻¹³
Cu ₂ S	2.24 x 10 ⁻⁴⁸		FeS	1.57 x 10 ⁻¹⁹		PbCO ₃	1.48 x 10 ⁻¹³
Fe(OH) ₃	2.67 x 10 ⁻³⁹		Fe(OH) ₂	4.79 x 10 ⁻¹⁷		Ag ₂ CO ₃	8.58 x 10 ⁻¹²
CuS	1.28 x 10 ⁻³⁶		Zn(OH) ₂	7.68 x 10 ⁻¹⁷		CdCO ₃	6.20 x 10 ⁻¹²
CdS	1.4 x 10 ⁻²⁹		Ni(OH) ₂	5.54 x 10 ⁻¹⁶		FeCO ₃	3.13 x 10 ⁻¹¹
PbS	8.81 x 10 ⁻²⁹		Cd(OH) ₂	5.53 x 10 ⁻¹⁵		MnCO ₃	2.23 x 10 ⁻¹¹
SnS	3.23 x 10 ⁻²⁸		Co(OH) ₂	1.09 x 10 ⁻¹⁵		NiCO ₃	1.45 x 10 ⁻⁷
ZnS	2.91 x 10 ⁻²⁵		MnS	4.55 x 10 ⁻¹⁴		MgCO ₃	1.15 x 10 ⁻⁵

It is notable that the metal sulfides are less soluble than metal hydroxides and carbonates. This metal sulfide solubility allows bioreactors to remove metals to low levels at neutral pH. Because bioreactors reverse the chemistry of sulfide oxidation, and the majority of the chemical added does not contribute mass to the sludge produced, the amount of sludge generated is reduced when compared to a neutralization technique where the chemicals added make up a large portion of the sludge that is generated. In addition, the passive to semi-passive nature of bioreactors allow for less management on site and reduced power needs, which both contribute to a lower overall cost.

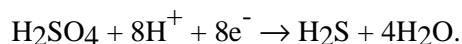
A simple flow-through design is generally utilized. ARD is gravity fed into a pond or tank that contains an organic substrate such as manure or wood chips. The ARD flows through the substrate where the treatment occurs and is released as water containing lower concentrations of metals with elevated alkalinity and pH. The substrate acts as a physical framework for metal sulfide precipitation and microbial attachment. In addition, the substrate serves as a carbon

source for growth and maintenance of sulfate-reducing bacteria. These reactors are promising as a less expensive, passive alternative to active treatment (lime precipitation).

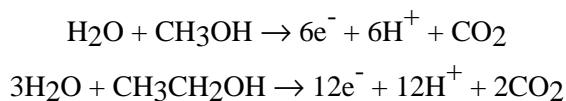
Limitations of Traditional Bioreactors

The problems associated with bioreactors in the past have been two-fold. First, the lifetime of a bioreactor is limited by the amount of carbon source readily available to sulfate-reducing bacteria. Once the source of carbon is exhausted from the substrate, sulfate-reducing bacteria will no longer efficiently reduce sulfate to sulfide and treatment efficiency decreases (Tsukamoto and Miller 1998). Second, substrates with small voids such as manure plug as the manure is degraded and metals are precipitated within the substrate. This causes short-circuiting and insufficient treatment.

Currently we are using bioreactors that utilize a carbon source that is added to the bioreactor influent. This type of system has the advantage of longevity, as well as allowing removal of specific concentrations of sulfate and metals based on stoichiometric addition of the carbon source. For example, the reduction of sulfate to sulfide requires 8 electrons:



Methanol and ethanol contribute 6 and 12 electrons, respectively, per molecule oxidized to carbon dioxide.



Electron accounting in this manner allows determination of the number of moles of carbon source needed to reduce one mole of sulfate, and can allow appropriate titrating of alcohol for the treatment needed.

In addition, when a liquid substrate is fed to the system as a carbon source, a matrix can be utilized which contains large pore spaces. This will increase hydraulic conductivity and reduce or eliminate plugging, particularly when a flushing mechanism is incorporated into the matrix.

The Leviathan Mine System

We have constructed and operated a bioreactor at the Leviathan Mine for approximately 4 years. The treatment system was designed as a dual cell bioreactor system. Cell 1 was approximately 2m deep x 7.3m wide x 17.3 m long, with a volume of approximately 175 m³. Cell 2 was approximately 2m deep x 10.7m wide x 17.3 m long, with a volume of approximately 292 m³. AMD can be distributed to cell 1 and cell 2 in parallel or in series, at any flow rate up to the total flow of the seep (approximately 30-60 L/min). AMD enters each cell from the surface and flows laterally through the cells where it is collected in 3 loops of perforated PVC pipe located at the bottom. Flows were initially controlled with valves.

Both cells were lined with 40 mil PVC that was covered with approximately 0.3 m of manure. The remainder of the substrate in cell 1 consisted of wood chips. Methanol was added as the source of reducing equivalents up to day 245 and a mixture of ethanol, methanol and ethylene glycol were added for the rest of the treatment period. The remainder of the substrate in cell 2 consisted of 6 to 20 cm cobble. Both cells were inoculated with an anaerobic horse manure culture upon filling the cells. Flows were maintained below 3L/min (total) up to day 237. At this time, the weir and standpipes were assembled and the flows were incrementally increased. Cells were run in series (i.e. the flow leaving Cell 1 entered Cell 2) and additional AMD was added to cell 2. Alcohol concentrations varied, but influent typically contained reducing equivalents to remove 1-3 times the amount of sulfate in solution.

Basic solutions were also added to the influent (to raise the pH for microbial growth) and effluent (for iron sulfide precipitation) following day 541 of the experiment. Influent solutions were typically increased to pH=3.8-4.3, effluent solutions were increased to pH 6.0-7.5. Following the addition of base we were able to increase flows dramatically while maintaining treatment.

Results From Leviathan Bioreactor

Trace metals (Ni, Cu, Zn) aluminum, iron and sulfate were effectively removed throughout the treatment period of 1200 days. Copper was removed from an average influent concentration of 0.82 mg/L to an average effluent concentration of 0.02 mg/L (figure 1). Nickel was removed from an average influent concentration of 0.41 mg/L to an average effluent concentration of 0.07 mg/L (figure 2). Zinc was removed from an average influent concentration of 1.82 mg/L to an average effluent concentration of 0.09 mg/L (figure 3). Iron was removed from an average influent concentration of 167 mg/L to an average effluent concentration of 3.75 mg/L (figure 4). Sulfate was removed from an average influent concentration of 1750 mg/L to an average effluent concentration of 1170 mg/L (figure 5).

Following the addition of base (day 541), flows were increased from an average flow of 1.6 L/min to 24.2 L/min. The entire flow of the seep was treated the majority of the time following base addition. Metals removal was maintained following base addition, while sulfate removal decreased only slightly despite shorter residence times within the reactor cells. Iron removal was dependant upon the effluent pH. When the effluent pH was maintained above 7.0, iron was typically removed to below 5.0 mg/L.

Costs Estimates

The costs associated with these bioreactors are dependent upon several factors including: flow, acidity, metals concentrations (specifically iron, aluminum, zinc), sulfate concentration, space available, temperature, and seasonal variations in all of the above.

The Leviathan Mine Bioreactor effectively treated flows of up 38-50L/min year round. The initial cost of the Leviathan Mine bioreactor was approximately \$120,000. The alcohol cost is approximately 75 cents/1000 gallons treated and the sodium hydroxide cost is approximately 22 cents/1000 gallons treated. Maintenance costs are generally less than \$5000/year excluding man-hours. Typically, frequent monitoring is required during acclimation and during the

production of a maintenance schedule. Monitoring once to twice per month may be sufficient once a schedule is determined. Typically, the sludge produced will pass hazardous waste disposal tests and therefore can be disposed of on site. If there is space available these disposal costs should be minimal.

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