Bioremediation of Acid Mine Drainage Using Sulfate-Reducing Bacteria

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LIST OF ABBREVIATIONS

ALD	Anoxic Limestone Drain
AMD	Acid Mine Drainage
AML	Abandoned Mine Lands
BEST	Bioreactor Economics, Size and Time of operation
BOD	Biochemical Oxygen Demand
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
HDPE	High Density Polyethylene
MOB	Manganese-Oxidizing Bacteria
MWTP	Mine Waste Technology Program
NOAA	National Oceanic and Atmospheric Administration
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
OLC	Open Limestone Channel
ORD	U.S. EPA Office of Research and Development
ORP	Oxidation-Reduction Potential
PCE	perchloroethylene
PRB	Permeable Reactive Barrier
RC	Reactive Cartridge
RTDF	Remediation Technologies Development Forum
SAPS	Successive Alkalinity Producing System
SRB	Sulfate-Reducing Bacteria
TCE	trichloroethylene
VOC	Volatile Organic Compound
TOC	Total Organic Carbon
TSS	Total Suspended Solid

1.   PURPOSE

This innovative technology report provides an overview of innovative acid mine drainage treatment technologies that employ sulfate-reducing bacteria (SRB). Through a synthesis of research and case studies of SRB treatment at coal and hardrock mine sites, it will present lessons for further application of this technology. The target audience for this paper includes owners, operators, contractors, regulators, and stakeholders with an interest in acid mine drainage remediation. Though this work focuses on abandoned hardrock mine sites generating acid drainage, aspects of these technologies may apply to active mine sites, coal mines, and other industrial operations that generate acidic and metallic discharges. These innovative remediation technologies are presented with the view of promoting more effective, efficient clean-up, or facilitating remediation of sites that could not practicably be treated with other technologies.

2.   INTRODUCTION

2.1 Nature of the Problem

Acid mine drainage occurs when mining activity brings sulfidic rock into contact with surface water or ground water. Under oxidizing conditions, pyrite-containing rock produces sulfuric acid and dissolved iron. These acidic waters may then dissolve other metals contained in the rock, resulting in low-pH, metal-bearing water known as acid mine drainage (AMD) or acid rock drainage (ARD). Neutral mine drainage, with circumneutral pH and high metal concentrations, may occur when carbonate minerals neutralize acidity

While the best way to minimize the impact of AMD is to avoid generating it, this option may not be available or entirely effective. This is the case for many abandoned mine lands (AML). The U.S. EPA AML Team defines abandoned mine lands as:

> *those lands, waters, and surrounding watersheds contaminated or scarred by the extraction, beneficiation or processing of ores and minerals (excluding coal[1]). Abandoned mine lands include areas where mining or processing activity is determined to be temporarily inactive.* (US EPA, 2004b)

It is difficult to quantify the size of the AML problem, due to different definitions of *site*, variation in inventory methods, the remoteness of many sites, and the uncertainty of impacts. Estimates of the number of AML sites in the U.S. vary from 200,000 to over 550,000 (US EPA, 2004b). Metal mining released 47 percent of all industrial toxins in 2000 (US EPA, 2004a).

The total cost of cleaning up pollution from AML sites is also difficult to quantify. The US EPA identified 156 hardrock mining sites that were on or had potential to be on the National Priorities List (NPL) for remediation under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), with the potential to cost between $7 and $24 billion to clean up

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[1] Though abandoned coal mines also generate AMD, coal mining in the U.S. is under the jurisdiction of the U.S. Department of the Interior, Office of Surface Mining. Due to this regulatory separation, this report will consider only hardrock mines in its definition of AML.

(US EPA, 2004a). A Mineral Policy Center estimate places the cost of reclaiming the worst 363,000 AML sites at \$32 to \$72 billion (US EPA, 2004b).

2.2 The Role of Innovative Technology

Given the potential for serious environmental damage and burdensome reclamation costs, it is practical to seek long-term, cost effective treatments for AMD. Passive treatment systems harness naturally-occurring processes to remediate contaminants. The potential advantages of passive treatment are lower costs, fewer site visits required, ability to work in remote areas, opportunities to use recycled or waste materials, and more natural appearance. Potential drawbacks include vulnerability to high flows and high contaminant concentrations, seasonal variation in performance, the need for periodic maintenance or renovation, space requirements, and the relative lack of technical experience with these systems.

Passive treatment systems for hardrock mine drainage involve chemical or biological acid neutralization and metals removal. Because diverse contaminants and environments require diverse treatment methods, various passive treatment technologies may be integrated. Like traditional waste water treatment plants, passive treatment systems often involve discrete components, or "cells" that perform a specific function or functions. The basic cell types are aerobic wetlands, open limestone channels (OLC), anoxic limestone drains (ALDs), anaerobic wetlands, and hybrids of these components, such as Successive Alkalinity Producing Systems (SAPS), bioreactors, and permeable reactive barriers (PRB) (Table 1). An alternative approach to passing water through a treatment system is to perform *in situ* treatment, by adding amendments to standing water, soil, tailings piles, or exposed rock surfaces. Amendments may serve multiple purposes, such as revegetation and soil stabilization, acid neutralization, contaminant immobilization, or stimulation of microbially-mediated alkalinity addition and metals removal.

For an overview of passive treatment technologies for acid mine drainage, see US EPA, 2005; Costello, 2003; Skousen, 1998; and Younger, 2000.

Table 1. Summary of passive treatment technologies

Technology Name	Technology Description	Function	Selected References
Aerobic wetlands	Shallow, surface flow wetlands with emergent vegetation	Fe and Mn oxidation and precipitation; co-precipitation of metals; sorption to biomass	Eger and Wagner, 2003; USDA and EPA, 2000
Open limestone channels	Acidic water flows over limestone, or other alkaline agent	Alkalinity addition; precipitation of Al, Fe, Mn as metal oxides	Ziemkewicz et al., 1997
Anoxic limestone drains	Water flows through limestone channel under anoxic conditions	Alkalinity addition; Fe precipitation; prevention of limestone armoring	Watzlaf et al., 2000
Anaerobic wetlands	Subsurface flow wetland, isolated from atmosphere by standing water or overlying material	Alkalinity addition; sulfate reduction and precipitation of metal sulfides; sorption or uptake by vegetation	Brenner, 2001; USDA and EPA, 2000
Successive Alkalinity Producing Systems	Vertical flow systems that drain through layers of limestone and anaerobic organic matter	Alkalinity addition; sulfate reduction and metal precipitation	Kepler and McCleary, 1994; Zipper and Jage, 2001
Sulfate-Reducing Bioreactors	Collected water drains into anoxic chamber containing organic matter and SRB	Alkalinity addition; sulfate reduction and metal precipitation	Gusek, 2002
Permeable Reactive Barriers	Intercepted groundwater flows through permeable barrier containing reactive material	Alkalinity addition; sulfate reduction and metal precipitation; sorption	Benner et al., 1997; US DOE, 1998
Amendments	Materials added to AMD sources or holding areas	Alkalinity addition; sulfate reduction and metal precipitation; sorption; chelation; revegetation	Chaney et al., 2000

3. TECHNOLOGY DESCRIPTION

3.1 Chemical Mechanisms of Treatment

This paper will focus on passive and semi-passive treatment technologies that employ sulfate-reducing bacteria (SRB). SRB are involved in several of the *in situ* and *ex situ* treatment technologies described above, and are often used in conjunction with other technologies. The general purpose of using SRB in AMD treatment is to produce sulfides for metal sulfide precipitation, while generating alkalinity.

The chemical basis of SRB remediation involves microbially-mediated sulfate reduction coupled with organic matter (represented by CH_2O) oxidation:

$$2\ CH_2O(aq) + SO_4^{-2} + H^+ \rightarrow H_2S + 2HCO_3^-$$
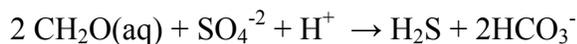
It also involves the chemical reaction of metal (Me) precipitation:

$$H_2S + Me^{+2} \rightarrow MeS + 2H^+$$
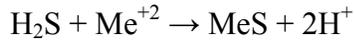
Cadmium, copper, iron, lead, mercury, nickel, and zinc are some of the metals that will precipitate as metal sulfides. In addition, arsenic, antimony, and molybdenum form more complex sulfide minerals (Figueroa, 2005). Metals such as manganese, iron, nickel, copper, zinc, cadmium, mercury, and lead may also be removed to some extent by co-precipitation with other metal sulfides (Figueroa, 2005). Furthermore, SRB species have been found that can reduce certain metals to a more insoluble form, such as reduction of uranium (VI) to uranium (IV) (Spear et al., 2000). Sulfate reduction also consumes acidity, raising the pH. Increasing the pH facilitates the above precipitation reactions and creates suitable conditions for precipitation of metal hydroxides (Gadd, 2004).

Because oxygen, nitrate, manganese and iron reduction all yield more energy per equivalent than sulfate, anaerobic conditions are required, and the oxidation-reduction potential (ORP) must be less than -200 mV to permit SRB to thrive and sulfate reduction to occur (Cabrera et al., 2006). These redox conditions are also suitable for iron reduction to the ferrous (Fe^{+2}) state, which will precipitate with sulfide.

3.2 Biological Characteristics of SRB

Sulfate-reducing bacteria are characterized by anaerobic respiration using sulfate as a terminal electron acceptor. They are classified into the following four taxonomic groups:
1. The δ-Proteobacteria subdivision contains Gram-negative mesophilic SRB, including the genera *Desulfovibrio, Desulfomicrobium, Desulfobulbus, Desulfobacter, Desulfobacterium, Desulfococcus, Desulfosarcina, Desulfomonile, Desulfonema, Desulfobotulus,* and *Desulfoarculus*. These bacteria have optimal growth temperatures ranging from 20 to 40°C. This group is diverse, with a variety of shapes and physiological traits represented.
2. The Gram-positive spore-forming SRB are mainly represented by the genus *Desulfomaculum*, and form heat-resistant endospores. Most species require a similar temperature range to Group 1, though some withstand higher temperatures.
3. The bacterial thermophilic SRB group contains the genera *Thermodesulfobacterium* and *Thermodesulfovibrio* These bacteria have optimal growth at 65 to 70°C, and inhabit high-temperature environments such as geothermal vents.
4. Archaeal thermophilic SRB thrive at temperatures above 80°C, and have been found only in marine hydrothermal vents. All SRB in this group belong to the genus *Archaeoglobus*. (Castro et al., 2000)

Sulfate-reducing bacteria inhabit a variety of sulfate-rich, reducing environments. High numbers of SRB have been found in lacustrine and wetland sediments, cattle rumens, and geothermal vents. They can also thrive in human-impacted environments such as rice paddies, paper mills, and streams impacted by sewage or acid mine drainage (Postgate, 1965). To stimulate

bioremediation, an SRB source such as cow manure or organic matter from one of the environments listed above is generally added to passive treatment systems.

While obtaining SRB is not difficult, passive treatment systems must create a suitable environment for them to ensure treatment success. An anoxic, reducing environment is one habitat requirement. Substrate, temperature, pH, and AMD chemistry may also impose limits, and have been the subject of laboratory and field studies. Some laboratory or bench-scale research is presented to supplement insight gained from field studies.

3.2.1 Substrate

Sulfate-reducing bacteria generally rely on simple carbon compounds such as organic acids or alcohols to serve as electron donors for sulfate reduction, though some are capable of using hydrogen (Logan et al., 2005). When organic matter is used as a carbon source, other heterotrophic bacteria must break it down into simple carbon compounds (Figure 1). Because the precise composition of organic matter is usually unknown, calculations of reducing equivalents may not be accurate. Bench- and pilot-scale studies using the intended carbon source and AMD to be treated are therefore critical to determine sulfate-reduction rates and design efficient, full-scale systems.

Figure 12. Microbial processes that can impact sulfate-reduction in an organic carbon substrate. Reprinted from Logan et al., 2005.

An alternative is to add simple carbon molecules, which require continuous addition due to their fast uptake rate. Both methanol and ethanol were effective liquid carbon sources in column experiments, and have been used in field applications (Tsukamoto et al., 2004).

The bioreactor or PRB fill material, referred to as "substrate" in this paper usually serves two purposes: to provide a carbon source and to maintain flow through the system. Because some materials do not serve both purposes well, mixtures of carbon sources with non-reactive material such as pea gravel are often used. In the case of liquid carbon sources, an entirely inorganic substrate may be used. In ethanol-fed columns, wood and rock matrices were associated with higher sulfate reduction rates and better adjustment to high flows than plastic substrate (Tsukamoto et al., 2004). Numerous laboratory and field studies have examined the suitability of various carbon sources and mixtures. Substrate performance will be further considered in the case studies presented in this report.

Column and batch studies showed that cellulose hydrolysis was a rate-limiting factor in hydrogen sulfide production by SRB, when more labile carbon sources were absent (Logan et al., 2005). Thus, if substrates are comprised largely of cellulose, which may be the case after long periods of treatment, cellulolytic bacteria exert a significant impact on SRB activity. Since cellulolysis is most effective at a pH of 6.0 or above, additional buffering may be required to utilize this substrate (Logan et al., 2005).

3.2.2 pH

Acid tolerance is beneficial in bacteria used to treat acidic drainage. It appears that SRB can survive in a wide range of pH conditions, but become less active below a certain pH. Jong and Parry (2006) found that SRB in laboratory scale bioreactors sustained sulfate reduction rates of 553-1052 mmol/m^3/day when the pH was lowered from 6.0 to 4.0. However, when the pH was lowered to 3.5, this rate dropped to 3.35 mmol/m^3/day. Similarly, SRB in ethanol-fed columns survived at the lowest pH tested (2.5), but were less effective at generating alkalinity below pH 3.0 (Tsukamoto et al., 2004). Acid-tolerant strains of SRB have been characterized and isolated, and their introduction to AMD treatment systems may improve performance (Johnson and Hallberg, 2005). However, a higher pH may be required for effective metal precipitation and organic carbon degradation, as described above.

3.2.3 AMD chemistry

Whether passive SRB treatment is sufficient to treat a particular AMD stream also depends on its chemistry. Up to a point, higher concentrations of metal lead to higher metal precipitation rates. Under these conditions, potential metal precipitation can be calculated from sulfate reduction rates and reaction kinetics. However, batch studies showed that high metal concentrations could slow bacterial population growth, decrease sulfate-reducing capacity, and ultimately cause death (Cabera et al., 2006). Mixed cultures of *Desulfovibrio* sp. tolerated higher concentrations than *Desulfovibrio vulgaris* alone, and were more likely to be representative of populations used in biotreatment systems (Cabrera et al., 2006). The EC100, or lowest dissolved metal concentration at which all sulfate reduction was inhibited, was 12 mg/L for copper, and 20 mg/L for zinc (Utgikar et al., 2001). Sulfate reduction was inhibited by 50% at EC50 values of 10.5 mg/L for copper and 16.5 mg/L for zinc (Utgikar et al., 2001). Laboratory tests showed that copper, cadmium, and nickel were toxic to a mixed culture of SRB at 20 mg/L, while zinc, chromium, and lead were less toxic, inhibiting sulfate reduction at 25, 60, and 75 mg/L respectively (Hao et al., 1994). Heterogeneous microenvironments available to SRB may mitigate this toxic effect in field applications.

3.2.4 Temperature

Low temperatures slow down SRB activity and thus reaction rates. In column experiments, SRB functioned effectively at 6°C, the lowest temperature tested (Tsukamoto et al., 2004). Cold-adapted species are able to function at temperatures as low as 4° C, and increased populations may offset lower activity (Higgins et al., 2003).

3.3 Implementation Considerations

Technology selection
The CERCLA feasibility study process is a useful framework for technology selection at a variety of remediation sites. The feasibility study considers effectiveness, implementability, and cost, as well as community and regulatory acceptance. This report will primarily focus on the *effectiveness* of passive treatment with SRB in a given situation.

Information required to identify potentially effective technologies includes (US EPA, 2005):
1. <u>AMD source characterization</u>: acid and metal loading, geochemistry, flow rates, etc.
2. <u>Site characterization</u>: topography, climate, risk of creating additional sources, etc.
3. <u>Environmental goals</u>: contaminants of concern, discharge standards, human or ecological risk criteria, ARARs, etc.
4. <u>Available technologies</u>: source control, active treatment, passive/semi-passive treatment

Guidelines for the selection of passive treatment technology have been summarized in a flow chart (Figure 2) created by Hedin et al. (1994), modified by Ziemkiewicz et al. (2003).
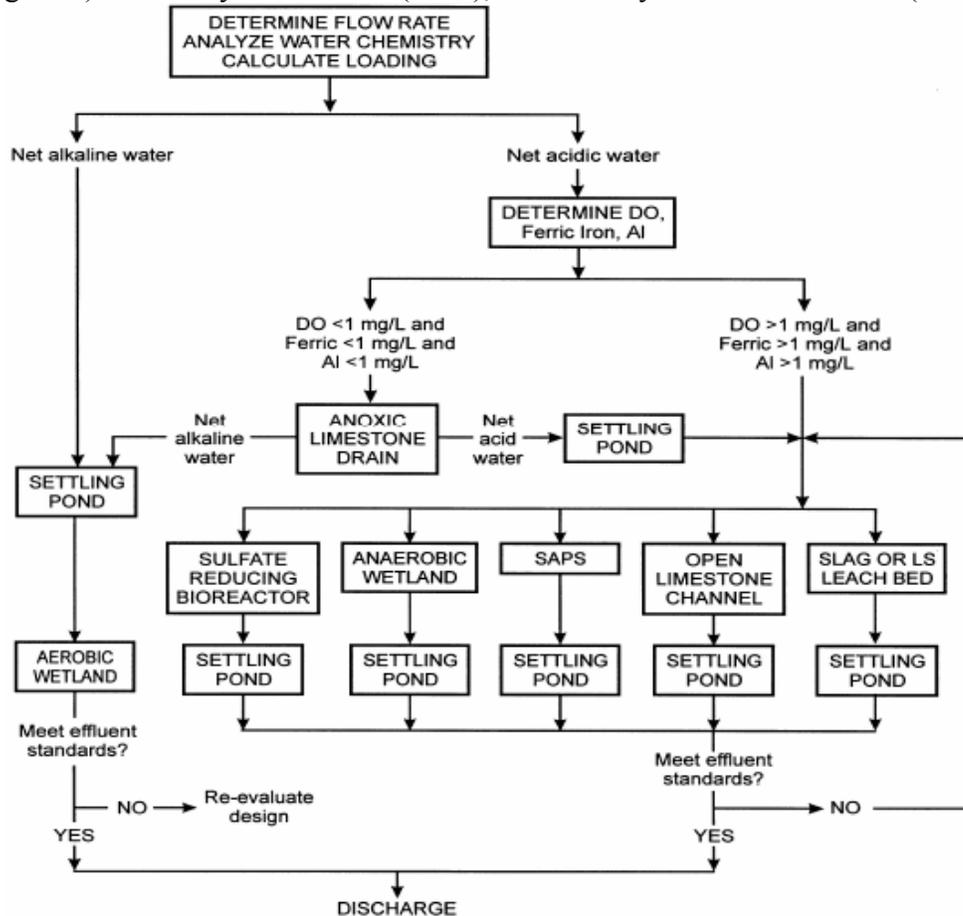
Figure 2. Diagram of possible passive treatment systems to treat mine water based on water flow and chemistry. Reprinted from Ziemkiewicz et al., 2003

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Design

Once a technology and application method (e.g., wetland, SAPS, or bioreactors for SRB) have been selected, site- and source-specific information can be combined with general design guidelines. No specific design is appropriate for every site; technical consulting, bench tests, and often pilot-scale tests are necessary to correctly size and configure passive treatment systems. However, general guidelines have been developed that may help guide the early stages of the design process.

The U.S. Bureau of Mines has established criteria for anaerobic wetland size, based on treatment of coal mine drainage. The Bureau recommends a minimum wetland size (in m^2) equal to the acidity loading (in g/day) divided by 0.7, and application to discharges with less than 300 mg/L acidity (PA DEP, 2006b). The recommended sizing based on iron removal is 10 g Fe/m^2/day (Skousen, 1998).

Design guidelines have also been promulgated for SAPS. The Pennsylvania Bureau of Abandoned Mine Reclamation recommends a design of 0.9 to 1.8 m (3 to 6 feet) standing water, 45 to 61 cm (18 to 24 inches) compost, and 45 to 61 cm (18 to 24 inches) limestone with drainage pipes, with a retention time of 12 to 15 hours in the limestone (PA DEP, 2006b). This guideline is fairly general, and a slightly different distribution of layers has been reported elsewhere (Demchak et al., 2001; Skousen, 1998).

For sulfate-reducing bioreactors, sizing depends on metal loading and acidity. Approximately 0.25 to 0.3 moles of sulfate reduction can be expected per m^3 per day (Gusek, 2002; MSE, 2006). More accurate sulfate reduction rates can be determined through bench tests using the AMD and organic matter to be employed. Stoichiometric calculations including AMD chemistry, desired removal rates, and a safety factor can be used to relate the sulfate-reduction level to metal loading. Surface area can be related to acidity with a guideline of 50 g acidity/day for each m^2 of area, though a more conservative estimate may be preferable (Gusek, 2005).

Models have been developed that integrate several of these characteristics, such as AMDTreat (developed for coal mine drainage), PHREEQC (geochemical modeling software), and BEST (developed for bioreactor design; see section 5.4.2).

4.   LESSONS FROM COAL MINING

Passive treatment technologies, including SRB, have been used to treat AMD from coal mines for over 20 years (Ziemkiewicz et al., 2003). The processes that generate AMD are the same for both types of mine. Like coal mines, most hardrock mines have potential to generate high acidity, sulfates, and metals, particularly iron, manganese, and aluminum. Therefore, there is much opportunity to learn from the history of passive treatment at active or abandoned coal mine sites.

The major categories of passive treatment involving SRB are constructed anaerobic wetlands, SAPS, sulfate-reducing bioreactors, permeable reactive barriers, and organic amendments. These SRB treatment systems or their precursors have been used at coal mine sites. The widespread application of SAPS (also known as vertical flow wetlands, or VFW) in treating coal mine drainage has been particularly informative, as SAPS involve principles and problems that are similar to other sulfate-reducing systems.

4.1 Performance

Several authors have evaluated the performance of multiple passive treatment systems, to develop general performance expectations (Brenner, 2001; Jage et al., 2000; Rose, 2006; Watzlaf et al., 2000; Ziemkiewicz et al., 2003). In one of the more comprehensive studies, 82 of 83 passive acid mine drainage treatment systems in the Eastern U.S. succeeded in reducing acidity. This study found that SAPS had an average acid removal rate of 62.3 $g/m^2/day$ and cost $253/ton/year, while anaerobic wetlands removed 24.5 $g/m^2/day$ and cost $527/ton/year on average (Ziemkiewicz et al., 2003). Though large variation in performance and cost made generalization difficult, this study showed that SRB treatment had potential to exceed accepted design factors of 20 g acidity/m^2/day for SAPS and 3.5 g acidity/m^2/day for anaerobic wetlands (Ziemkiewicz et al., 2003).

4.2 Challenges and Innovations

From years of experience with passive treatment, coal mine remediation specialists have had the opportunity to encounter numerous problems and potential remedies. Problems with passive treatment systems for coal mine drainage include discovering additional flows during construction, leakage, water level control, excessive odor, and greater maintenance requirements than anticipated (PA DEP, 2006a). The following issues have also been associated with SRB treatment at both coal and hardrock mine sites, and are addressed in several case studies.

Seasonal declines in SAPS performance from November to April were attributed to decreased microbial activity and increased flow from snowmelt (Brookens et al., 2000). A seasonal trend in sulfate reduction was also observed at Howe Bridge and Pot Ridge SAPS, though not at other SAPS included in these studies (Rose et al., 2001; Watzlaf et al., 2000).

While vertical flow wetlands typically remove iron and aluminum fairly efficiently, manganese removal rates are often low (Brookens et al., 2000; Watzlaf et al., 2000). Since the reducing conditions and pH in SRB-mediated processes are often not appropriate for manganese

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treatment, additional design features that promote manganese removal are highlighted in some of the following case studies.

Maintaining reducing conditions is critical to SRB effectiveness, but has not been achieved in all SAPS. An insufficiently thick compost layer may cause this problem (Rose et al., 2001). An organic matter layer at least 50 cm thick has been recommended, based on depth at which reducing conditions were found in SAPS studies (Demchak et al., 2001). An anaerobic wetland system reverted to aerobic conditions due to low substrate permeability, resulting in low system performance (Skousen et al., 1999).

Clogging of pipes or substrate has also plagued many vertical flow systems, necessitating periodic repair or maintenance (Rose et al., 2001; Brookens et al., 2000). The prevalence of flow problems has led to design innovations, such as flushing systems (Weaver et al., 2004). A semi-passive recirculating SAPS has also been designed to precipitate hydroxides in an aerobic detention pond outside the SAPS, reducing stress on the organic matter layers (Garrett et al., 2001).

Because high aluminum concentrations lead to gibbsite formation, which tends to clog ALDs and SAPS, sulfate-reducing bioreactors have been constructed at abandoned coal mines that discharge high-aluminum AMD (Gusek and Wildeman, 2002). Though the mechanism of aluminum removal differs from typical metal sulfide precipitation and is incompletely understood, there is evidence that these systems prevent gibbsite formation (Gusek and Wildeman, 2002). The following case study is one situation in which bioreactor treatment effectively replaced a problematic SAPS. It also illustrates a watershed-based approach to AMD remediation
.

4.3 Case Study: Yellow Creek Phase 2B Bioreactor

Site History
Blacklick Creek Watershed is a 1,090 km^2 (420 mi^2) watershed in Western Pennsylvania. The watershed contains 300 surface coal mines and 170 coal refuse dumps, which contribute an average of 136,000 kg (300,000 lbs) of acid per day to the streams. (Black Creek Watershed Association, 2006).

Since its formation in 1993, The Blacklick Creek Watershed Association (BWCA) has made it a priority to abate the impacts of AMD on the main stem of Blacklick Creek and its tributaries. To this end, the BWCA has worked with public and private partners to remediate AMD sources in each of the nine subwatersheds. The BWCA strategically plans remediation projects from the headwaters to the mouth of each tributary, to restore the water quality and trout fisheries that once existed in the area. (R. Eppley, pers. comm., 2006)

The Lower Yellow Creek Restoration Project in Indiana County, Pennsylvania began in 1998. The project has been funded by Section 319 NPS grants, Western Pennsylvania Watershed Protection funds, and Commonwealth of Pennsylvania Growing Greener grants. This 5-phase plan aims to restore a 5.6 km (3.5 mi) section of Yellow Creek, one of the major tributaries to Blacklick Creek (AMR Clearinghouse, 2004). Five treatment systems have been constructed

between 1998 and 2003. The three SAPS initially in place did not effectively treat the drainage, and experienced plugging due to high aluminum concentrations (Gusek, 2005). The systems currently in place have all been upgraded to or constructed as sulfate-reducing bioreactors. (AMR Clearinghouse, 2004)

One passive treatment system included in this project is the Phase 2B bioreactor at Judy 14 Coal Mine, an underground mine that has been abandoned since the 1950's (Gusek, 2005). During the time of treatment, AMD entering the Yellow Creek Treatment System Phase 2B (YCTS) has had an average pH of 2.8, 574.7 mg/L acidity, 45 mg/L iron, 33 mg/L aluminum, 2.6 mg/L manganese, and 791.7 mg/L sulfate (Kiski-Conemaugh Stream Team, 2006; Gusek, 2005). The goal for the treatment is compliance with Pennsylvania Department of Environmental Protection effluent standards, including pH between 6.5 and 8.5, less than 1 mg/L aluminum, and less than 1 mg/L iron (R. Eppley, pers. comm., 2006).

Technology Application
The YCTS sulfate-reducing bioreactor was built in 2002, based on positive results of a pilot system treating similar drainage. Part of the water exiting the Judy 14 mine shaft is diverted through a valved pipe into the demonstration sulfate-reducing bioreactor. The bioreactor pond has a 0.13 ha bottom area and is 0.76 m deep. It is lined with one foot of compacted clay. The substrate is comprised of 50% wood chips, 30% limestone, 10% cow manure, and 10% hay. On exiting the bioreactor, the effluent combines with the effluent of another bioreactor and flows through a wetland settling system and rock filter before discharging to Yellow Creek. The bioreactor was designed for an average flow rate of 38 L/min (10 gpm). The construction cost of the system, including engineering design, was $158,000. (Gusek, 2005)

The YCTS, along with other treatment systems and AMD discharges in the Kiski-Conemaugh Watershed, are being monitored monthly by the Kiski-Conemaugh Stream Team. Funded by the Pennsylvania Department of Conservation and Natural Resources, the Stream Team is comprised of volunteers who monitor water chemistry at 191 sampling points. These data are disseminated via the website: http://www.kcstreamteam.org. (Kiski-Conemaugh Stream Team, 2006)

Results
The YCTS is in its fourth year of operation, and continues to reduce sulfate, generate alkalinity, and lower iron and aluminum concentrations. Manganese concentrations showed little to no change. The effluent has consistently met water quality standards, with a pH of 6.6, and at least 99% removal of aluminum, iron, and nickel (Table 3; Gusek, 2005). The bioreactor receives approximately 45 L/min (12 gpm) discharge on average (Kiski-Conemaugh Stream Team, 2006).

Table 2. Yellow Creek 2B bioreactor, water chemistry

Analyte	Influent	Effluent
pH	3	6.6
Al	33	0.07
Cu	0.1	<0.009
Fe	45	0.5
Mn	2.6	2.3
Ni	0.32	0.002
Zn	0.86	0.06

Data from Gusek, 2005; All concentrations in mg/L

Lessons Learned
- Sulfate-reducing bioreactors can lower dissolved metal concentrations and acidity over a period of several years, even under high-aluminum conditions.
- Effective manganese removal requires a different type of system.
- Community groups acting in partnership with states can play a critical role in addressing the many smaller sources of AMD in the watershed.

Site Contacts
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5. HARDROCK MINING CASE STUDIES

5.1 Sulfate-Reducing Bioreactors

Like SAPS, sulfate-reducing bioreactors (bioreactors) harness the chemical and biological processes associated with sulfate reduction in anaerobic wetlands, using designs engineered to maintain desired conditions. They may also incorporate chemical alkalinity addition through mixture of limestone or other alkaline agents into the substrate. In this paper, bioreactors are distinguished from constructed anaerobic wetlands by the lack of emphasis on wetland characteristics, such as wetland vegetation and surface flow. However, some of these systems may be described as wetlands by other sources. The term *bioreactor* may also be appropriate to distinguish systems designed for wastewater treatment from constructed wetlands designed to provide habitat and related ecosystem services. Passive treatment systems that are more appropriately described as anaerobic wetlands are in use at Copper Basin, TN (Faulkner and Miller, 2003) and Tenmile Creek, MT (Reisman et al., 2005).

5.1.1 Case Study: Wheal Jane Pilot Passive Treatment Plant

Site History
The Wheal Jane mine is located in the Carnon Valley, Cornwall, UK. The mine site is approximately seven miles southwest of the town of Truro. The area receives an average of 1042 mm of rain per year, and has an average temperature of 10-12° C (Met Office, 2006).

Tin and other metal mining took place at Wheal Jane for several hundred years before its closing in 1991. After the mine's closure, mine shafts and workings filled with ground water, dissolving sulfidic, metal-rich rock. In 1992, an adit plug failed and about 50,000 m^3 of acid mine drainage was released to the Fal Estuary and Carnon River, causing serious environmental damage. (Hallberg and Johnson, 2003). The contaminated water was extremely acidic, and contained high concentrations of iron, zinc, cadmium, and arsenic. Iron hydroxide formation left a yellow-orange precipitate on the beds of the water bodies. This highly visible, widely reported event drew attention to the need for remediation, and emergency pumping and treatment were instituted (CL:AIRE, 2004).

In 1994, passive treatment facilities were built to investigate the potential of this technology to treat mine drainage before it reached the Carnon River (Whitehead et al., 2005). The project was funded by a LINK grant from the UK Department of the Environment, with additional support from industrial partners. The UK Environment Agency has oversight of this mine and treatment plant (Whitehead and Prior, 2005).

An active lime treatment plant capable of treating all discharge from Wheal Jane began operation in 2000. However, the passive treatment system was renovated and studied intensively by researchers from several universities from 2000 to 2002, to assist in developing new remediation approaches (CL:AIRE, 2004). The passive system is no longer operational due to lack of funding.

Technology Application

The Wheal Jane passive treatment system received mine water from Jane's Adit through an underground piping system (Whitehead et al., 2005). The mine adit feeding the Wheal Jane Pilot Passive Treatment Plant (PPTP) during the 2000-2002 study period had a pH of 3, and dissolved concentrations of 161.3 mg/L iron, 12.4 mg/L aluminum, 41.9 mg/L zinc, and 1,094 mg/L sulfate on average (Table 3; Whitehead, 2006).

The system was designed to treat 36 L/min (9.5 gpm), and could receive peak flows of up to 114 L/min (30.1 gpm) (CL:AIRE, 2004). The plant contained three multi-cell treatment systems that utilized one of three pre-treatment methods to raise pH: lime dosing to pH 5.0 with calcium carbonate (LD), an anoxic limestone drain (ALD), or a lime-free system without pretreatment (LF). Due to plugging, the ALD system was modified to function as another lime dosing system. In each treatment system, the pre-treated drainage passed to aerobic reed bed wetlands for iron and arsenic removal. Next, water flowed through an anaerobic cell for sulfate reduction and heavy metals removal. The final stage was an aerobic rock filter, designed to promote manganese removal (Figure 3). (Whitehead and Prior, 2005) This case study focuses on the anaerobic cells' performance, and the contribution of SRB to overall water quality improvement. Further references to LD, ALD, and LF systems refer to the entire treatment path, not just the pretreatment components.
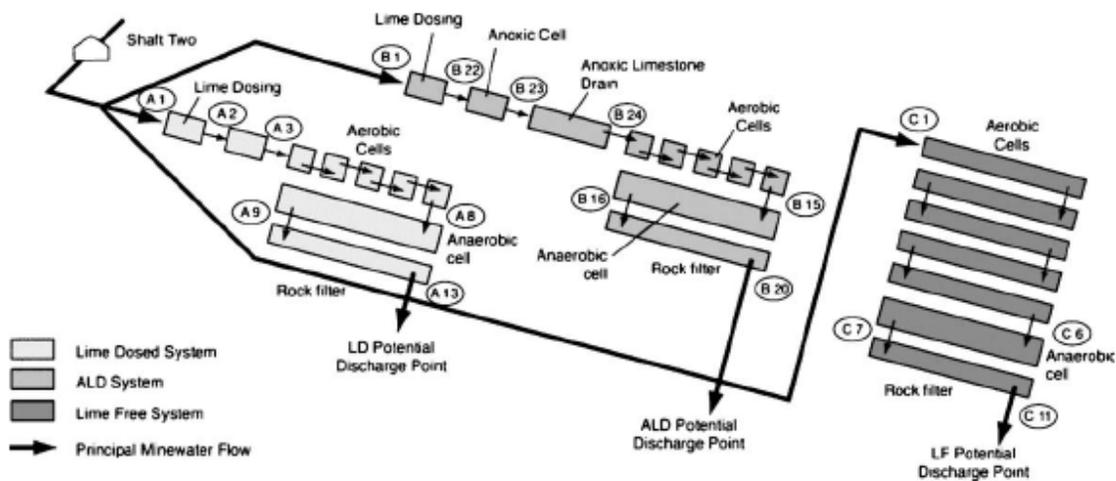
Figure 3. Schematic of Wheal Jane PPTP. Reprinted from Whitehead and Prior, 2005.

The anaerobic wetland cell at Wheal Jane PPTP was entirely below ground and lacked wetland macrophytes, and thus may be more appropriately characterized as a compost bioreactor. The anaerobic cell in each system was approximately 87.5 m long, 8.75 m wide, and 1 m deep, lined with high-density polyethylene (HDPE) membranes. This depression contained a mixture of 95% softwood sawdust, 5% hay, and a small quantity of cow manure to inoculate the bioreactor with SRB. The mixture was covered with approximately 0.4 m of earth and gravel, to maintain anaerobic conditions. (Johnson and Hallberg, 2005)

The anaerobic cells were designed with sufficient organic matter for a 30-year lifetime, when functioning properly. They were sized based on a volumetric metal loading rate of 0.3 moles metal per m^3 per day. The surface area was determined by a surface area loading factor of 20 m^2 per liter per minute. (Whitehead et al., 2005)

System maintenance was minimal during the study period. Pilot cells began operation in 1995, and the compost in the bioreactors was replaced in early 2000. The LF system was shut down due to a fracture in the main influent pipe between August 2000 and June 2001. (Johnson and Hallberg, 2005) All results refer to the operational period from June 2001 to September 2002, unless otherwise stated.

Construction of the system cost £1 million (about $1.7 million), and operational costs were approximately $100,000/year. Monitoring costs were approximately $150,000/year, primarily for detailed chemical analysis. (Whitehead, 2006).

Results

The bioreactors were constructed primarily to generate alkalinity, raise pH, and remove heavy metals, particularly zinc. The influent AMD from the aerobic wetlands was similar for each system, with a pH between 3 and 4, and 95 to 100% dissolved oxygen saturation. Redox potential and dissolved oxygen concentrations decreased in all three bioreactors. (Johnson and Hallberg, 2005)

Table 3. Wheal Jane PPTP, water chemistry for entire system, 2000-2002

Analyte	Influent	LD	ALD	LF*
pH	~3	4.5	5	6.8
Al	12.4	10.4	12.4	2.2
Cu	0.1	0.051	0.096	0.071
Fe	161.3	2.5	4.2	0.4
Mn	5.3	7.3	7.3	0.83
Pb	0.1	0.037	0.066	0.986
Zn	41.9	9.9	23.6	1.7
Sulfate	1094	1015	890	435

Data from Whitehead, 2006; All concentrations in mg/L
*System shut down from March-June 2001; no data for this period

Table 4. Wheal Jane compost bioreactor water chemistry, 2001-2002

	LD		ALD		LF	
Analyte	influent	effluent	influent	effluent	influent	effluent
pH	3.6	5.5	3.6	5	3.9	5.9
Fe	3.8	17.3	5.8	12.6	3.6	0.4
Zn	36.4	16.3	29.7	9.8	40.7	0.01
Sulfate	245	205	230	184	233	128
ORP (mV)	768	178	743	222	741	66

Data from Johnson and Hallberg, 2005; All concentrations in mg/L

All three bioreactors increased pH, to 5.5 (LD system), 5.0 (ALD system), and 5.9 (LF system). When discharged to the rock filters, pH decreased to 4.5 in the LD and 5.0 in the ALD systems, while it increased to 6.8 in the LF system (Table 3). Oxidation of excess sulfide and ferrous iron from the bioreactor effluent may have contributed to the downstream pH decrease. (Johnson and Hallberg, 2005) The low pH in the bioreactor effluent and rock filters likely contributed to the failure of manganese removal in the LD and ALD systems (Whitehead et al., 2005).

Sulfate concentrations decreased in all three bioreactors over the treatment period. During the entire monitoring period, the bioreactors lowered sulfate concentrations by 27±18% (LD), 23±12% (ALD), and 62±20% (LF). The bioreactor in the LF system consistently removed the most sulfate. However, its efficiency decreased from 91% to 39% over the study period. In all systems, sulfate concentrations increased from bioreactor effluent concentrations in the rock filter. (Johnson and Hallberg, 2005)

Like sulfate, zinc was removed in all bioreactors, though the LF system bioreactor had the greatest removal rate (Table 4). Based on September 2002 measurements, the bioreactors removed 55% (LD), 67% (ALD), and 99% (LF) of soluble zinc. Dissolved zinc concentrations increased in the rock filter in the ALD system, but decreased in the other systems (Johnson and Hallberg, 2005). However, data collected from March 2000 to February 2002 showed removal rates over 99% for the LD system (Table 3; Whitehead, 2006).

Though much soluble iron was removed in the pre-treatment and aerobic cells, concentrations continued to change in the anaerobic bioreactors. Soluble iron in the LD and ALD bioreactor effluent was more than twice the influent (Table 4). Soluble iron decreased within the LF system bioreactor and generally remained low. All three complete treatment systems ultimately lowered soluble iron concentrations by at least an order of magnitude. (Johnson and Hallberg, 2005)

Microbiological evidence indicated a low level of SRB establishment in the bioreactors. The dominant bacteria cultivated from effluent samples were acidophilic iron-oxidizers. SRB colonies were rare, except in the LF bioreactor on the February 2002 sample date. The low level of SRB establishment in two of the bioreactors affected overall system performance. Though excess sulfide was produced in all three bioreactors, it did not effectively form iron sulfide precipitates in two bioreactors, apparently due to the low pH. Furthermore, ferric iron minerals entered the bioreactors and were reduced to soluble ferrous iron, increasing dissolved iron within two of the bioreactors. Sulfides and ferrous iron exported in the bioreactor effluent were then oxidized to sulfate and ferric iron, increasing acidity downstream. (Johnson and Hallberg, 2005)

Lessons Learned
Johnson and Hallberg (2005) attribute the poor performance of the anaerobic cells to the following factors:
- Acidic, oxygenated water entering the bioreactors created suboptimal conditions for SRB growth.
- SRB populations were unable to tolerate the acidity of the system. A ten-month shutdown of the LF system may have allowed more tolerant microbial populations to develop and flourish in the anaerobic cell.

- Soluble and particulate ferric iron entering the bioreactors exceeded the capacity of the system to reduce and precipitate iron, particularly under low-pH conditions.
- Collection of rainwater in aerobic cells added unnecessarily to the flow entering the bioreactors.

Based on the results of this experimental pilot plant, the following recommendations for compost bioreactor construction have been developed:
- Place compost bioreactors upstream of aerobic cells, to avoid introducing oxygenated, highly acidic AMD into the bioreactor.
- Avoid collection and treatment of excess rainwater in system components.
- Allow bioreactors time to develop healthy SRB and other microbial populations before beginning AMD flow through the bioreactor.
- Inoculate bioreactors using SRB sources likely to contain more tolerant bacteria, such as those found in AMD-impacted sediments. (Johnson and Hallberg 2005)

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5.1.2 Case Study: Doe Run West Fork Mine Bioreactor

Site History
The West Fork Mine Site is an active underground lead-zinc mine in Reynolds County, Missouri, located in the New Missouri Lead Belt. This region of Missouri has an average annual temperature of 13° C, and average annual precipitation of 1110 mm (NOAA, 2002).Water from mine drainage flows into the West Fork of the Black River.

The West Fork Unit was transferred from ASARCO to the current owner, Doe Run, in 1998. Both owners have utilized the sulfate-reducing bioreactor to treat water pumped from the mine shaft. The mine water discharged to the West Fork of the Black River must comply with water quality standards set forth in the West Fork Unit's NPDES (National Pollutant Discharge Elimination System) permit. Mine water is discharged at about 4540 L/min (1,200 gpm), and contains average concentrations of 0.6 mg/L lead, 0.08 mg/L zinc, and 180 mg/L sulfate (Gusek, 2005). Treatment was required to meet the NPDES discharge limit of less than 0.035 mg/L for lead (Gusek et al., 1998). A passive treatment system was chosen based on feasibility assessment and lower costs than active treatment.

Technology Application
Bench tests and field tests preceded full-scale bioreactor construction. Bench tests consisted of placing substrate (cow manure and aged sawdust) in eight-foot diameter "bio-tanks", and introducing mine water flow at a rate of 7.9 L/min (2.1 gpm). (Gusek et al., 1998)

The substrate remaining from the bench test was used to inoculate the pilot scale bioreactor, which operated from March 1994 to February 1996. The pilot scale system was a bioreactor built next to the mine site, designed to receive 76 L/min (20 gpm) flows. Flows up to 185 L/min (49 gpm) were passed through the bioreactor to test different operational scenarios. The pilot scale system achieved lead concentrations below 0.02 mg/L, meeting all discharge standards. (Gusek et al., 1998)

The full-scale system was constructed adjacent to mine and mill buildings, a tailings pond, and the West Fork of the Black River. Water is pumped from an underground mine shaft into a settling pond, then flows by gravity through the rest of the system. The major components of the system include a settling pond, two parallel anaerobic cells, a rock filter, and an aeration pond (Figure 4). It was built to accommodate 4540 L/min (1,200 gpm) nominal flow, and 5680 L/min (1,500 gpm) maximum flow. The entire system covers 2 ha of land. If the organic substrate is utilized at the same rate as in the pilot scale
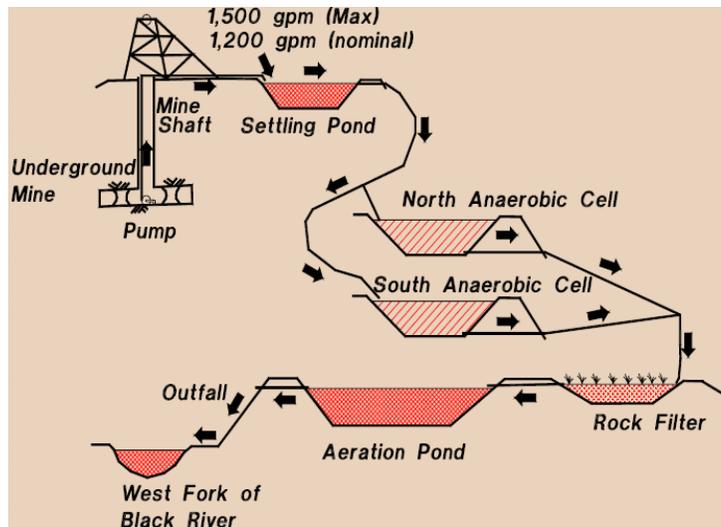

Figure 4. Schematic of the passive treatment system at West Fork Unit, Doe Run Mine. Reprinted from Gusek, 2005.

bioreactor, the lifetime of the treatment system should be greater than 30 years. (Gusek et al., 1998)

The anaerobic cells (bioreactors) are lined with 40-mil HDPE and have a surface area of 0.19 ha each. Four sets of fluid distribution pipes and three sets of fluid collection pipes are connected to layers of perforated pipe and geonet for fluid distribution (Gusek et al., 1998). The bioreactor is filled with layers of 67% sawdust, 19% inert limestone, 12% composted cow manure, and 2% alfalfa mixture, with a total thickness of approximately 1.8 m (Gusek, 2005). This substrate is covered with a layer of crushed limestone. The bioreactors discharge into an internally baffled concrete vault, which provides mixing and flow control (Gusek et al., 1998).

During normal operation, an anaerobic bioreactor may discharge water containing manganese, high biochemical oxygen demand (BOD), fecal coliform bacteria, sulfides, and low dissolved oxygen. A 0.23-hectare, 0.3-meter deep rock filter cell, with limestone cobble lining and berms, is intended to improve these aspects of water quality. Algae and cattails have been added to the rock filter to enhance oxygenation and carbon uptake. In particular, the bacteria *Leptothrix discophora* facilitates precipitation of manganese as manganese oxide. A 0.32-hectare aeration pond further decreases BOD and provides dissolved oxygen polishing prior to discharge into the receiving stream. (Gusek et al., 1998)

The system began operation in 1996, and continues to treat mine water. At start-up, the anaerobic cells were incubated with settled mine water for 36 hours, to minimize BOD, fecal coliform, and manganese release. Pumps then recycled water within the anaerobic cells for two weeks. (Gusek et al., 1998)

The total cost for construction was $500,000. Design and permitting costs added $200,000. (J. Gusek, pers. comm., 2006).

Results

After eight years of operation, the bioreactor system continues to discharge water that meets NPDES permit requirements. Effluent lead concentrations range from 0.027 to 0.05 mg/L. Zinc concentrations are less than 0.05 mg/L. Sulfate is also removed, with average concentrations less than 140 mg/L. The system maintains a pH of approximately 7.8. (Gusek, 2005) The system has produced high-quality effluent year-round, indicating that sulfate reduction rates are sufficient during cold months (J. Gusek, pers. comm., 2006).

One problem encountered after six weeks of operation was a loss of substrate permeability in one of the anaerobic cells. Hydrogen sulfide gas was being trapped beneath the geotextile layers, blocking vertical flow. To release the gas and restore flow, the cells were ultimately excavated and refilled without mid-cell geotextile layers, preventing further gas locks. (Gusek et al., 1998)

In later years, the downflow anaerobic cell experienced clogging due to formation of an algal mat. This problem was treated and prevented by periodically rototilling the substrate. Eventually, emergent vegetation growing in the cell shaded the surface, suppressing algal growth. (J. Gusek, pers. comm., 2006)

The bioreactors were also threatened by plugging when changes in mine operation caused suspended solids to enter the anaerobic cells. The porosity was increased by increasing the proportion of woodchips in the organic substrate, allowing flow to be maintained. (J. Gusek, pers. comm., 2006)

Lessons Learned
- Sulfate-reducing bioreactors are a viable means of removing lead in neutral mine drainage, even in high flows.
- Bench-scale and pilot-scale tests can facilitate proper sizing, substrate selection, and operation of full-scale bioreactors.
- Flow problems may result from hydrogen sulfide locks, algal growth, or introduction of particles; therefore, it is desirable to have access to the substrate for renovation or maintenance.
- Anaerobic bioreactors must be supplemented with other technologies such as rock filters or aerobic polishing ponds, to remove manganese, BOD, and fecal coliform bacteria, and restore dissolved oxygen to the discharge.

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5.1.3 Case Study: Lilly/Orphan Boy Mine In Situ Bioreactor

Site History
The Lilly/Orphan Boy Mine is an abandoned lead mine, located 11 miles south of Elliston, Montana. This location is characterized by difficult access, heavy snow, and rapid snowmelt, yielding high flows in spring. The average temperature in this region of Montana is 6° C, and the average annual precipitation is 370 mm (NOAA, 2002).

The project site is an abandoned mine shaft, mined in the 1940's and 1950's. The mine shaft is 75 m deep, connected to four horizontal tunnels. Upsurging ground water fills the shaft to approximately 23 m below the shaft opening. The mine discharges AMD through a horizontal tunnel and portal at this elevation (Figure 5). The discharge flows into a tributary of the Clark Fork River at an average rate of 11 L/min (3 gpm). Water quality concerns include elevated aluminum, arsenic, cadmium, copper, manganese, iron, zinc, sulfate, and acidity (Table 5). (Canty et al., 2001)
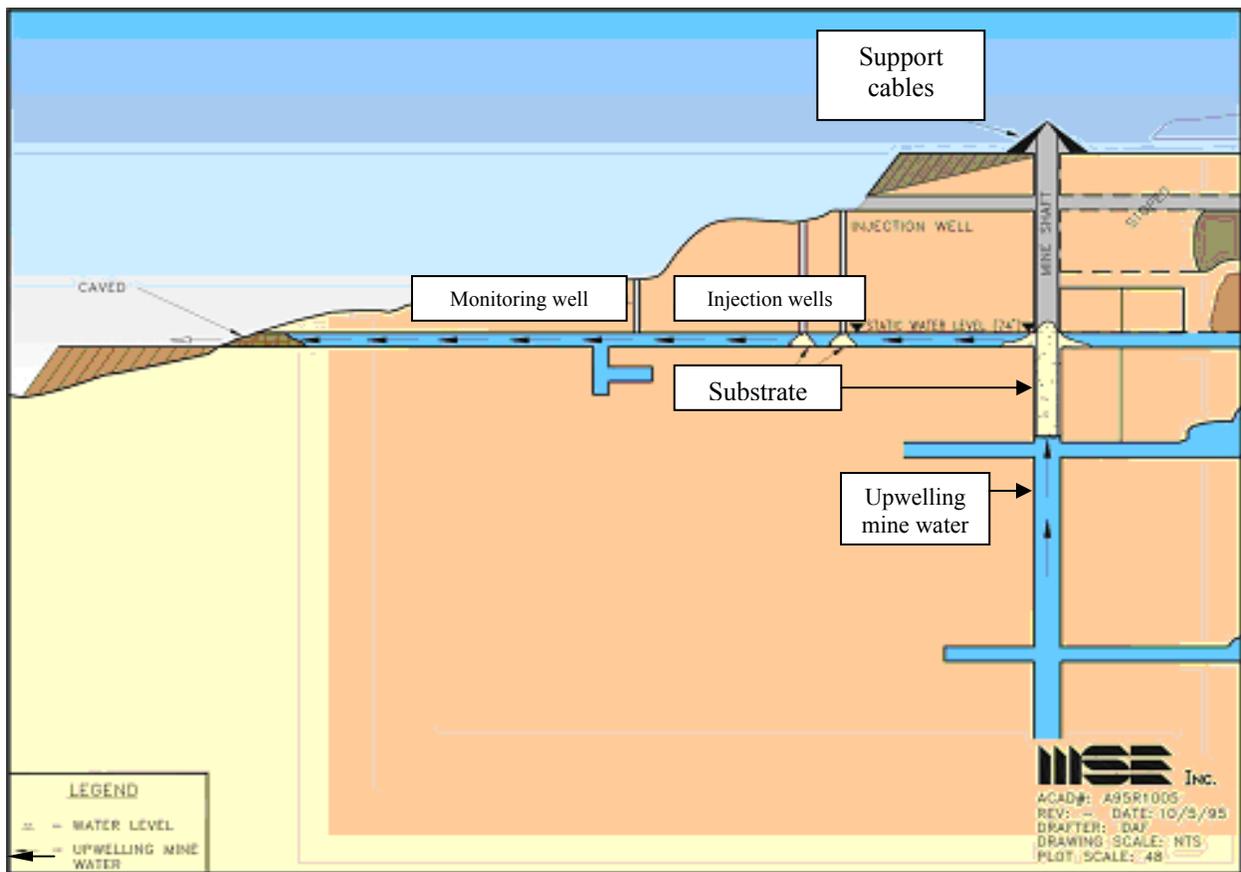

Figure 5. Cross-section of Lilly/Orphan Boy Mine. Adapted from MWTP, 2004.

Technology Application
In 1994, an *in situ* bioreactor was constructed within the Lilly/Orphan Boy mine shaft, as a demonstration project under Activity III, Project 3 of the Mine Waste Technology Program (MWTP). The MWTP is funded by the U.S. EPA and jointly administered by the U.S. EPA and

U.S. Department of Energy (DOE). The bioreactor was monitored from 1994 to 2005, and is still in place.

The bioreactor was built within the mine shaft, providing a permeable organic substrate for sulfate reduction mediated by SRB. Platforms were suspended in each part of the two-compartment shaft at a depth of 9 m below the ground water surface/tunnel level. These support platforms were suspended from cables secured at the surface near the mine opening. This created a two-compartment bioreactor, supported by the platforms and the walls of the mine shaft. The flow path through the bioreactor was upward through approximately 9 m of substrate, exiting horizontally through the tunnel. The temperature in the mine shaft was approximately 8°C. (Canty et al., 2001)

The substrate consisted of a mixture of manure, hay, and woodchips, dominated by manure. Two injection wells were drilled in the tunnel near the bioreactor, for the addition of substrate, but no substrate has been added to date (D. Bless, pers. comm., 2006).

Effluent was monitored at two points: through a monitoring well drilled to the tunnel, and from discharge through the mine portal. Due to the difficulty of sampling ground water before upwelling through the bioreactor, concentrations are compared to those prior to bioreactor construction. However, samples taken in the area near the bioreactor confirm that the untreated water in the mine is acidic, metal-rich, and under reducing conditions (S. Nordwick, pers. comm., 2006).

Results
Effluent water chemistry averaged over ten years shows that the bioreactor was effective at raising pH and decreasing most metal concentrations (Table 5). Samples from the well near the bioreactor indicate that the *in situ* bioreactor removed nearly all of the aluminum, arsenic, cadmium, copper and zinc, and raised the pH to near neutral. Iron and magnesium concentrations were reduced by 65% and 76%, respectively. (MWTP, 2004)

Metal concentrations increased and pH decreased between the tunnel sampling point and the portal, indicating additional exposure to acid-generating rock or AMD input from fractures in the tunnel (Table 5). Iron and arsenic concentrations in the portal effluent were higher than background levels. Magnesium concentrations were only 12% lower than background. Moderate amounts of zinc (52%) and large percentages of cadmium, copper, and aluminum (80-95%) were removed. (MWTP, 2004) Like most sulfate-reducing bioreactors, this demonstration bioreactor did not effectively remove manganese, averaging less than 20% removal. (Canty et al., 2001) In the portal effluent, only copper concentrations were low enough to meet primary or secondary maximum contaminant levels.

The water chemistry of portal effluent also varied seasonally. During spring runoff, pH at the portal fell to 3.5. Metal concentrations were higher in portal effluent during runoff, even for metals with typically high removal efficiencies, such as aluminum, cadmium, and copper. Within the mine tunnel, pH was maintained at 7 and metal concentrations were consistent throughout the year. (Canty et al., 2001)

Table 5. Lilly/Orphan Boy Mine bioreactor chemistry, 1994-2004

Analyte	Untreated AMD	Tunnel Effluent	Portal Effluent
pH	3	7	6
Al	9.69	bdl	0.51
As	1.07	0.04	3.66
Cd	0.33	bdl	0.064
Cu	0.32	bdl	0.041
Fe	27.7	9.7	28.4
Zn	26.1	bdl	12.5

Adapted from MWTP, 2004

All concentrations in mg/L; bdl=below detection limit

Lessons Learned

- Constructing an *in situ* bioreactor within a mine shaft is a passive treatment technology that involves minimal cost, maintenance, and space requirements, which may be suitable for remote, abandoned mine shafts.
- Consistent, upwelling ground water flowing through the bioreactor was able to sustain sulfate reduction and metal precipitation over at least ten years, without apparent clogging or substrate depletion.
- Water quality of the discharge was not optimal in this design, due to additional exposure of treated effluent to acid mine drainage within the tunnel. This could be remedied in future projects by conducting geophysical analysis of the area prior to construction to identify fractures or "hot spots" that will generate AMD. This information can increase effectiveness by application to siting bioreactors, grouting fractures, or otherwise immobilizing contaminants (S. Nordwick, pers. comm., 2006).
- Variable flow negatively impacted bioreactor performance and water chemistry. The impact of high flows could be addressed through enhancements such as valves to the bioreactor or storm ponds for water storage (S. Nordwick, pers. comm., 2006).

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5.1.4 Case Study: Surething Mine Integrated Bioreactor

Site History
Surething Mine is an abandoned metals mine, approximately 11 miles south of Elliston, Montana. The site elevation is approximately 2200 m 7200 feet above sea level. This location is characterized by difficult access, heavy snow, and rapid snowmelt, yielding high flows in spring. The average temperature in this region of Montana is 6° C, and the average annual precipitation is 370 mm (NOAA, 2002).

Surething Mine was mined for gold, zinc, silver and lead from the 1800's through the 1950's. The 137-meter abandoned mine shaft has been inactive since that time. The mine adit discharges ARD to O' Keefe Creek, a tributary of Telegraph Creek, in the Clark Fork River Basin. The mine water contains elevated aluminum, arsenic, cadmium, copper, iron, lead, manganese, zinc, sulfate, and ammonia (Table 6). It is also highly acidic, with a pH of approximately 2.6. (Bless et al., 2006)

This site was chosen for a pilot-scale demonstration of innovative technologies for AMD treatment or prevention. The study was conducted under Activity III, Project 16 of the Mine Waste Technology Program (MWTP). The MWTP is funded by the U.S. EPA and jointly administered by the U.S. EPA and U.S. Department of Energy (DOE).

Technology Application
The demonstration treatment at Surething Mine took place from 2001 to 2005. After testing sulfate-reducing bacteria capabilities at bench scale, an integrated treatment system was constructed in summer 2001. The entire system relied on gravity-driven flow, and was designed for 7.6 L/min (2 gpm) discharge. Actual discharge reached peaks of 38 L/min (10 gpm) during spring runoff.

The integrated system employed both aerobic and anaerobic components to treat target contaminants and raise pH (Figure 6). Water passively flowed from the mine adit to the first system component, an anaerobic bioreactor. This cell contained an organic mixture of 50% (by volume) cow manure and 50% walnut shells, combining labile and recalcitrant carbon sources. The cow manure also served as the source of SRB. This bioreactor was designed to create reducing conditions that would stimulate SRB,
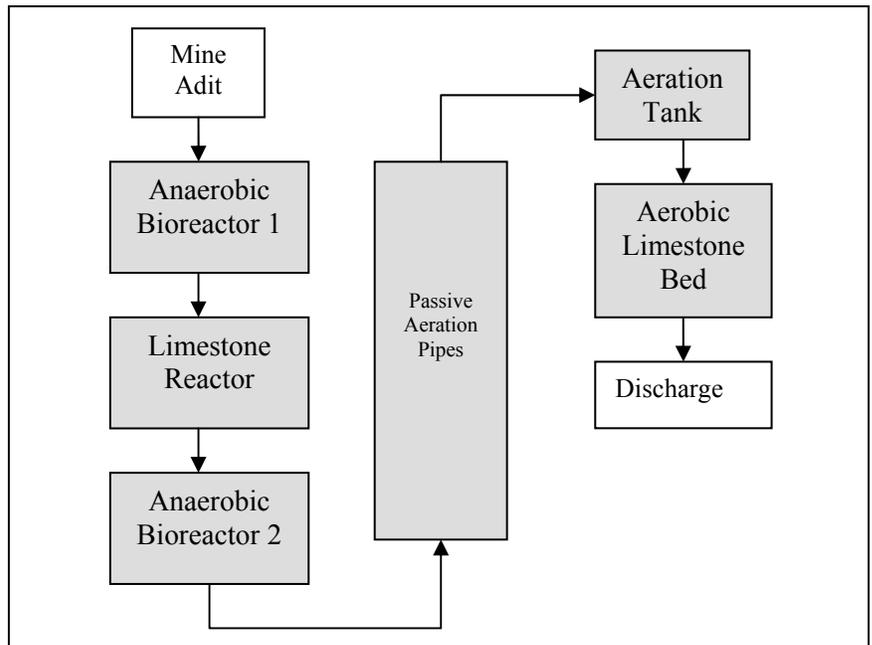

Figure 6. Configuration of the Surething Mine Integrated Passive Treatment System. Adapted from US EPA, 2005.

generating sulfides and alkalinity. (Bless et al., 2006) The bioreactor had an approximate 3-day residence time at 7.6 L/min, and contained 112 m^3 (146 yd^3) of organic matter. The surface of the cell was covered with alfalfa for insulation. (B. Park, pers. comm., 2006)

The anaerobic bioreactor effluent entered a second anaerobic reactor, which contained 41 m^3 (53 yd^3) of limestone cobbles to increase alkalinity. The limestone reactor had a residence time of approximately 1.3 days, and was also insulated with an alfalfa covering (Park, 2006). Reduction of ferric iron in the previous bioreactor would prevent ferric iron precipitates from armoring the limestone in this cell.

The third bioreactor, with the same organic mixture as the first bioreactor, was designed to remove metals through metal sulfide precipitation. This bioreactor was somewhat larger than the first, with 84 m^3 (110 yd^3) organic substrate and a two day residence time. It was also insulated with an alfalfa covering. (B. Park, pers. comm., 2006) Effluent from this bioreactor was aerated in 91 m (300 ft) of corrugated pipe, containing small barriers to promote mixing. The effluent was then held for two to three hours in an above-ground aeration tank, to restore oxygen and eliminate excess sulfides. (Bless et al., 2006)

The final bioreactor was an aerobic, baffled limestone bed for manganese removal. Based on a design guideline of 0.5 g/m^2/day and an estimated loading of 141.5 g/day, the limestone bed was designed to have a surface area of 279 m^2 (B. Park, pers. comm., 2006). With a depth of one meter, the original settling pond was too deep to provide sufficient aeration for manganese-oxidizing bacteria. The addition of a liner and additional limestone layer on top of the existing substrate increased the effectiveness of this aerobic reactor (D. Bless, pers. comm., 2006).

Construction costs for the system were approximately $250,000. Performance and equipment functionality were monitored monthly during the demonstration period. (Bless et al., 2006)

Results

In its final configuration, the system removed 92% to over 99% of each metal, and yielded water that met all Montana water quality standards for contaminants of concern (Table 6). Sulfate concentrations were lowered approximately 60%. The pH of the effluent was circumneutral.

Table 6. Surething Mine treatment system water chemistry, 2005

Analyte	Feed Concentration	Discharge Concentration	State Standard
pH	2.58	7.31	6.5-8.5
Al	29.5	<0.04	0.087
As	0.127	<0.01	0.01
Cd	0.208	<0.00009	0.00076
Cu	2.35	<0.003	0.037
Fe	15	<0.014	0.3
Pb	0.151	0.004	0.015
Mn	26.7	0.037	0.05
Zn	22.7	<0.007	0.338
NH4-N	0.11	0.37	4.61
Sulfate	591	239	250

Adapted from Bless et al., 2006; All concentrations in mg/L

Ammonia concentrations increased due to passage through nitrogen-rich organic matter, but remained below state standards. The anaerobic portions of the system effectively treated aluminum, arsenic, cadmium, copper, iron, lead, and zinc. In four years of operation, the passive treatment system treated three million gallons of AMD. (Bless et al., 2006)

Manganese does not readily precipitate as a sulfide mineral, and therefore was not effectively treated by SRB activity in the anaerobic system. The corrugated pipe, aeration tank, and aerobic reactor were designed to establish aerobic conditions that would be favorable for manganese-oxidizing bacteria (MOB). Originally, the system removed 95% of the manganese, but this removal rate dropped in winter and eventually remained at low levels. It was inferred that the MOB were harmed by excess sulfide carried over from the anaerobic portion of the system. (MWTP, 2004) To remove this sulfide, aeration capacity was added in 2003 and 2004 by adding 61 m (200 ft) of corrugated pipe and decreasing the depth of the aerobic reactor as described above. These modifications resulted in 99% manganese removal rates. (Bless et al., 2006)

The system also had problems with iron precipitates plugging the pipes in the first bioreactor and entering the limestone cell. Plugging was reduced by replacing and reconfiguring the piping system. The new feed system included a manifold of three vertical pipes with perforations, to enhance horizontal flow within the bioreactor. The pipes were also removable, allowing periodic cleaning. (B. Park, pers. comm., 2006)

Though final samples indicate the system as a whole remained effective, the first bioreactor showed signs of failure. Bench-scale tests indicated that the first bioreactor would fail before the rest of the system, due to stress imposed on SRB by the low-pH feed (Bless et al., 2006). After three years, aluminum and iron concentrations leaving the first bioreactor were similar to the influent AMD. At the conclusion of the study, the first bioreactor was able to raise the pH from 2.58 to 4, and remove copper, cadmium and zinc (B. Park, pers. comm., 2006). A final report on the system will be issued in 2006 by the EPA Office of Research and Development.

Lessons Learned
- A combination of sulfate-reducing bioreactors and limestone treatment can effectively remove iron, aluminum, and several other metals, while raising pH.
- Separate treatment systems are most likely necessary if manganese treatment is required. An aerobic reactor that stimulates manganese-oxidizing bacteria is a viable option.
- Feed systems should be configured to allow maintenance, as plugging may impede flow through the piping. Design features that promote even flow distribution, such as perforated vertical pipes, can also improve bioreactor function.
- Exposure to AMD with high metals and acidity limits bioreactor lifetime.

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5.1.5 Case Study: Leviathan Mine Compost-Free Bioreactor

Site History
Leviathan Mine is an abandoned copper and sulfur mine near Markleeville, California. The mine site is located 2134 m (7,000 ft) above sea level in the Sierra Nevada Mountains. The mine pit and waste cover 101 ha. (US EPA, 2004) This site is characterized by long, cold, snowy winters, during which the site is only accessible by snowmobile. The area receives an estimated 706 mm precipitation annually. Half of the runoff from the site comes from melting snow in the spring. (US EPA, 2006)

Intermittent mining activity at Leviathan began in the 1860's, and open pit mining took place at Leviathan from 1952 to 1962. Water quality problems became apparent in the 1950's, when an acid mine drainage release killed fish and insects in Leviathan Creek, Bryant Creek, and the Carson River. This prompted investigation of the impacts of Leviathan Mine on receiving streams. In the 1980's the State of California began the Leviathan Mine Pollution Abatement Project, which reduced impacts significantly by collecting and diverting surface water, regrading, filling, constructing storage and evaporation ponds, and installing channel under drains. In 1997, EPA initiated enforcement actions to begin mitigation of remaining AMD sources. As a result, California installed an active lime treatment plant to treat collected mine water. (US EPA, 2006) In 2000, Leviathan Mine was placed on the National Priorities List (US EPA, 2004).

Generation of sulfuric acid from Leviathan lowered the pH of discharge to 4, and degraded nine miles of stream system. Arsenic, copper, iron, nickel, and zinc were the primary metals of concern. Cadmium, chromium, lead, selenium, and zinc were the secondary water quality indicator metals designated for this project. Concentrations of the five target metals have been up to 3,000 times greater than the EPA interim discharge standards. (US EPA, 2006)

Previous actions had not addressed the AMD flowing from Aspen Seep into Aspen Creek. A compost-free bioreactor was designed to treat this source. Aspen Seep has relatively moderate characteristics, with historically high iron (124 mg/L) and aluminum (51mg/L) concentrations, and other metal concentrations near or less than 1 mg/L. (US EPA, 2006)

Technology Application
Bench and pilot-scale studies by the University of Nevada-Reno led to development of a semi-passive, liquid carbon source bioreactor system to treat Aspen Seep. The full-scale system began operating in spring 2003 and was evaluated through 2005. The bioreactor is currently in place and undergoing further development.

Gravity-Flow Mode
The technology implemented at Leviathan Mine consists of a pretreatment pond, two bioreactors, two continuous-flow settling ponds, and an aeration channel (Figure 7). Aspen Seep discharge flows in through a flow control weir, with inflow ranging from 22.2 to 82.9 L/min (6.4 to 21.9 gpm). The AMD is combined with a 25% sodium hydroxide solution, raising the pH from 3.1 to 4.0. This reduces stress on microbial populations in the bioreactor. Ethanol is also added to serve as a carbon source for SRB. The liquid mix flows into the 28 m^3 pretreatment pond for

mixing, flow stabilization and some metal precipitation. The pretreatment pond has a residence time of approximately four hours. (US EPA, 2006)

Three influent lines feed the pretreated influent through the first of two bioreactors in series. The first bioreactor is a 150-m^3, 60 mil HDPE-lined pond, filled with 23 to 40-cm diameter river rock, providing a nonreactive, porous substrate for SRB. A manure layer covers the bottom of the cell, inoculating it with SRB. This bioreactor is a primary source of sulfide for metal precipitation. The hydraulic residence time of the bioreactor is approximately 22 hours. The second bioreactor has the same basic design and materials as the first, but a smaller volume (85 m^3) and a residence time of about 13 hours. (US EPA, 2006)

Additional 25% sodium hydroxide is added prior to the continuous-flow settling pond to neutralize residual acidity, convert bisulfide to sulfide, and promote metal hydroxide precipitation. This settling pond is 455 m^3 and has a residence time of approximately 68 hours. From the pond, treated water passes to a rock-lined channel, where it is aerated before discharge to the stream. Alternatively, AMD can pass into a second settling pond for system flushing or additional settling time. The entire system required 3,000 m^3 of space to treat 114 L/min of drainage. (US EPA, 2006)

Recirculating Mode
This system can be operated as described above or in recirculating mode (Figure 7). In this mode, the bioreactors serve mainly as a sulfide source, and metal precipitation occurs externally in the settling ponds. The pH of water entering the bioreactors is raised to approximately 7.0, fostering optimal microbial activity. These changes are designed to promote more efficient metal removal and reduce stress on the bioreactors due to flushing. (US EPA, 2006)

In recirculating mode, AMD is routed from Aspen seep directly to the continuous-flow settling pond, where it mixes with sulfide-rich bioreactor effluent and 25% sodium hydroxide solution, and then flows to the second settling pond. Sulfate-rich, metal-poor pond supernatant is then pumped to a holding pond, ethanol is added, and the influent mixture (1:2 to 1:6 influent AMD to recirculated water) is routed through the bioreactors. The water entering the bioreactors is near neutral and low in metals. (US EPA, 2006)

The second continuous-flow settling pond was added after the first one to allow system flushing. Water flushed through the bioreactors can enter this flushing pond and remain there for extended settling of precipitates. This may be particularly necessary in gravity flow mode, as precipitate accumulation in the bioreactors can hinder performance. It has also been important under high flow conditions, providing extra sludge storage and settling time. (US EPA, 2006)

Operation & Maintenance
At start-up, each bioreactor was allowed to acclimate for two months by initially introducing low flows and gradually increasing to full flow. From November 2003 to mid-May 2004, the bioreactor system treated the entire flow of Aspen Seep in gravity-flow mode. During this period, system maintenance occurred approximately one to two days a week. The pretreatment pond was flushed monthly, with 2,000 to 7,000 L of solids transferred to the flushing pond each month. The bioreactors were flushed every two months, with approximately 15,000 L of solids

removed each time. Once during operation, 32,000 L of sludge was transferred from the first settling pond to the second settling pond. (US EPA, 2006)

From mid-May 2003 through 2005, the bioreactor system was operated in recirculating mode. Maintenance occurred one to two days a week. The bioreactors were flushed every three or four months, with 15,000 L of solids transferred each time. In accordance with the design, most solids deposition occurred in the first settling pond. Before winter, approximately 48,000 L of sludge were transferred from the first settling pond to the second, to ensure sufficient volume was available in the first pond. Operation in recirculating mode required 49% less sodium hydroxide and 14% more ethanol per liter treated than gravity-flow mode. (US EPA, 2006)

In 2005, sludge accumulated from both modes of operation was removed from the first settling pond by pumping it into 10' by 15' filter bags. The total removed was 200,000 L, or approximately 5.0 tonnes (5.5 dry tons) of solids. After a season of especially high flows, both ponds will need to be pumped again in 2006 (Tsukamoto and Miller, 2006). This sludge was found to be non-hazardous by RCRA and California hazardous waste standards, and the filter bags were disposed of on site (US EPA, 2006). While pumping into filter bags prevents disturbing more sensitive system components, it provides imperfect separation of fine particles, and resuspends sediments in the process (K. Mayer, pers. comm., 2006). A new system is being developed with a settling pond that can be emptied, so solids can dry prior to collection (G. Miller, pers. comm., 2006).

Table 7. Operational parameters of Leviathan bioreactor system, 2003-2005

Parameter	Gravity-flow mode	Recirculation mode
Flow rate (L/min)	31.8	34.2
Ethanol delivery (mL/min)	13.7	105
NaOH delivery (mL/min)	35.3	14.1
Hydraulic residence time (hours)	650	298

Data from US EPA, 2006

Cost
The construction cost of the system was $836,600 for the gravity-flow system or $864,100 for the recirculating system, with an average operation and maintenance cost of $19.45 per 1,000 gallons treated (Bates et al., 2006).

Results
The Leviathan Mine Bioreactor removed 95% of all target metals in two years of operation. Four of the five target metals met the EPA interim water quality discharge standards. Iron did not meet the standards overall, but did so when an optimal level of base was added. The bioreactor reduced sulfate concentrations by 17%. The pH of discharge was raised from 3.0 to 7.0. Table 8 shows metal removal rates in both gravity flow and recirculation modes. (US EPA, 2006)

Table 8. Leviathan Mine bioreactor system metal concentrations, 2003-2005

Gravity Flow Configuration			
Analyte	**Average influent concentration**	**Average effluent concentration**	**Interim Discharge Standard (Avg.)**
Al	37.467	0.103	2.000
As	0.002	0.005	0.150
Cu	0.691	0.005	0.016
Fe	117.167	4.885	1.000
Ni	0.487	0.066	0.094
Cd	0.0006	<0.00021	0.004
Cr	0.012	0.008	0.310
Pb	0.0036	0.0047	0.005
Se	0.014	0.011	0.005
Zn	0.715	0.016	0.210
Recirculation Configuration			
Analyte	**Average influent concentration**	**Average effluent concentration**	**Interim Discharge Standard (Avg.)**
Al	40.029	0.053	2.000
As	0.007	0.007	0.150
Cu	0.795	0.005	0.016
Fe	115.785	2.704	1.000
Ni	0.529	0.070	0.094
Cd	0.0006	<0.00020	0.004
Cr	0.011	0.006	0.310
Pb	0.0042	0.0025	0.005
Se	0.012	0.008	0.005
Zn	0.776	0.009	0.210

Adapted from US EPA, 2006; All concentrations in mg/L

As mentioned above, iron removal was problematic in this system, exceeding the average discharge criteria of 1.0 mg/L. One cause for this was experimentation with different amounts of base addition. When base addition was optimized, it appeared possible to meet discharge standards (US EPA, 2006). Though iron removal rates were about 99% by 2005, concentrations exceeded discharge criteria on one occasion when high flows led to in sufficient base addition. It exceeded standards again when the base delivery pump lost power and failed to deliver sodium hydroxide. (Tsukamoto and Miller, 2006)

The high flows in 2005 (50% greater than 2004) also provided a natural test of the limits of the system. High flow rates led to more metal loading and chemical consumption. Though the system continued to perform well overall, metal precipitate accumulation rates were higher than expected, creating a need for sludge removal two years in a row, after almost three years of operation with no sludge removal. (Tsukamoto and Miller, 2006)

The bioreactor exhibited slower biological activity during the winter. Lower flows during times of snow cover coincided with the decreased activity, allowing water quality standards to be met year-round (Bates et al., 2006). The bioreactors' three-meter depth kept SRB active in freezing conditions, since the ground was not frozen below 0.6 m (US EPA, 2006). It is worthwhile to note that all other alternative systems, such as active lime treatment, were forced to shut down during the winter season (Tsukamoto and Miller, 2006).

While methanol and ethanol were used in the 2003 to 2005 study period, alternative carbon sources are currently being tested. Biodiesel production waste, which contains methanol, triglycerides, sodium hydroxide and potassium hydroxide, is being investigated, as it provides cost savings and recycles a waste product. It could also reduce base addition requirements. (G. Miller, pers. comm.)

Lessons Learned
- A liquid carbon source bioreactor with a rock matrix can effectively remove metals from AMD through sulfate reduction.
- A recirculating mode that combines bioreactor-generated sulfides with base and AMD can be used to precipitate metals in a settling pond, reducing bioreactor flushing requirements and the consequent stress on SRB. This should also increase the long-term sustainability of treatment.
- Adjusting pH to at least 4.0 optimized SRB activity, while neutral pH in the settling pond increased metal removal efficiency. Sodium hydroxide was preferable for base addition, due to its solubility, low freezing point, and small dosage requirements. However, safety factors make minimization of its use desirable.
- Precipitate accumulation required periodically flushing ponds or bioreactors, allowing solids to accumulate in settling ponds, and removing settled solids from ponds by pumping. More efficient sludge removal techniques would facilitate the waste disposal process.
- Having extra pond capacity for sludge transfer or additional solids settling time can reduce frequency of flushing, allowing the system to function in higher flows or prolonged freezing conditions.
- Low temperatures may reduce SRB activity. The impact of this decrease can be mitigated by designing bioreactors with extra sulfate-reducing capacity, controlling winter flows, and constructing bioreactors with sufficient depth to prevent freezing throughout.
- Treating AMD at remote sites presents a challenge, as no effective, maintenance-free system has been found. This semi-passive treatment system has the advantages of low power requirements, resistance to freezing, and good recovery if maintenance lapses. However, it still requires weekly to biweekly maintenance, and storage of sodium hydroxide and fuels.

Figure 1-2. Flow Schematics With Recycle

Pretreatment Pond   Recycle Line

Aspen seep   Bioreactor 1   Bioreactor 2   Settling Pond 1   Settling Pond 2

Bypass Line

Ethanol Delivery

Sodium Hydroxide
Delivery

Oxidizing Aeration
Trench

Infiltration Pond
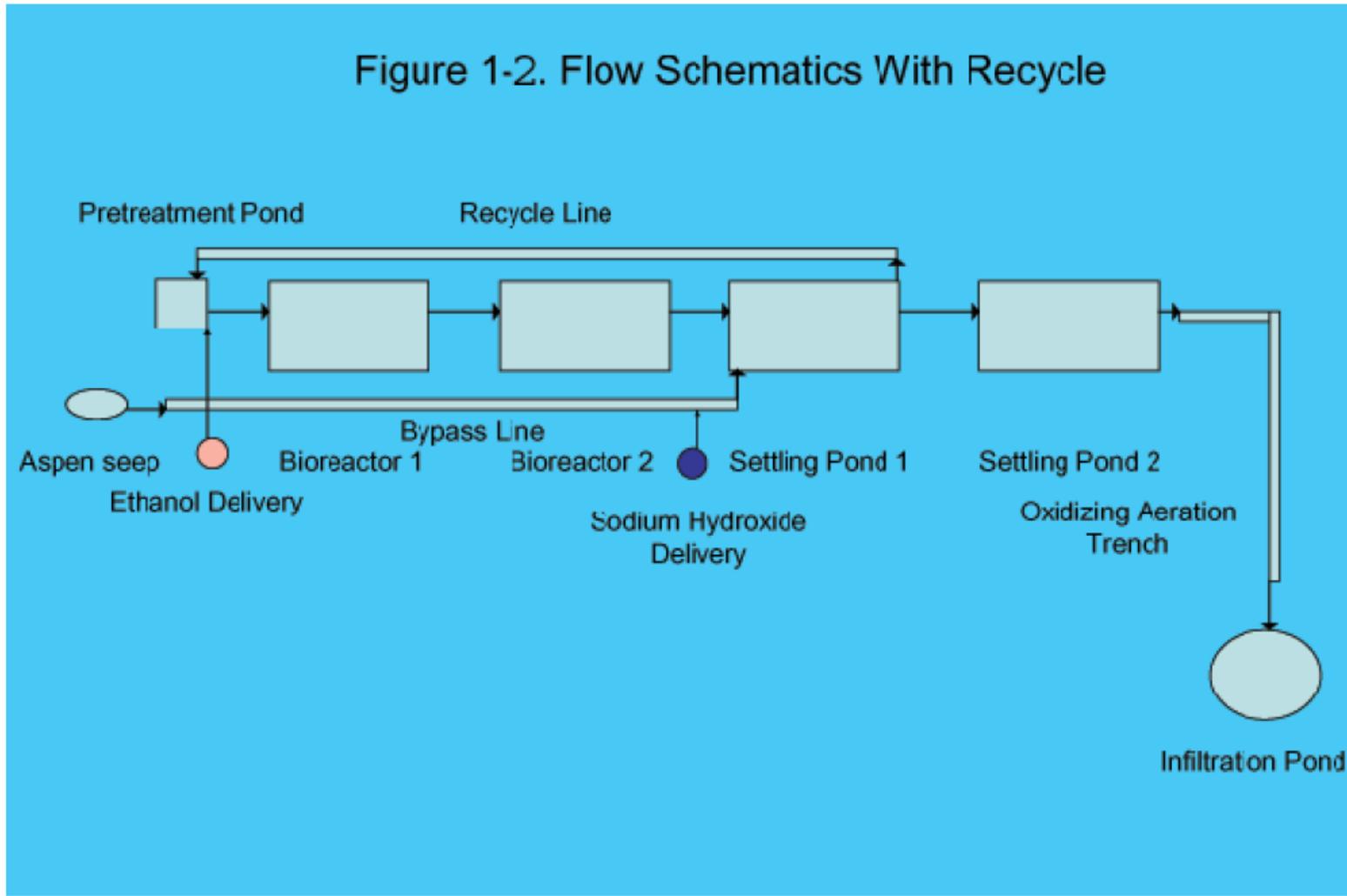
Figure 7. Configuration of Leviathan Mine Compost-Free Bioreactor system and flow path in recirculation mode. Reprinted from Tsukamoto and Miller, 2006.

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5.2 Permeable Reactive Barriers

When mine drainage flows through the subsurface, it is advantageous to employ SRB treatment to ground water, before iron oxidation and a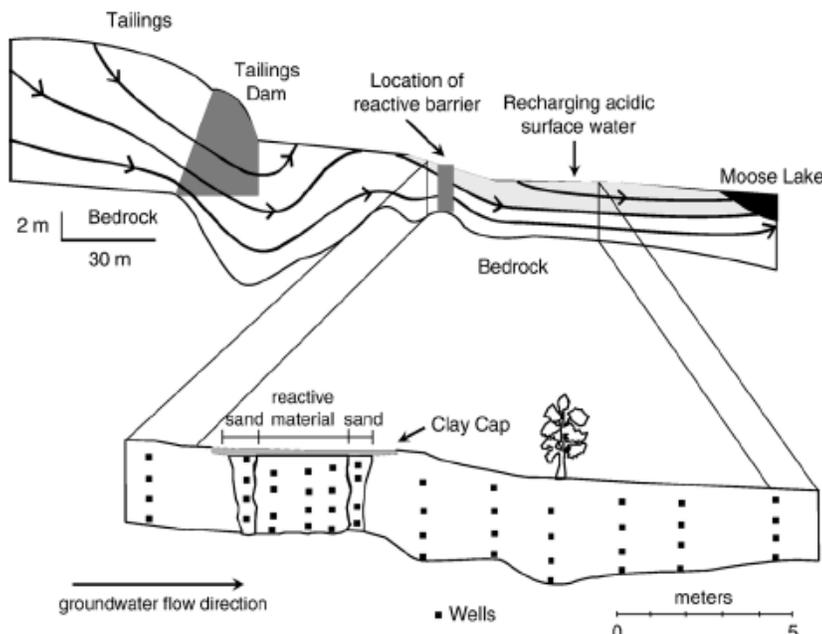cid generation occur. Permeable reactive barriers have been used to passively treat ground water containing organic and inorganic contaminants such as PCE, TCE, VOCs, radionuclides and metals (DOE, 2000). These barriers may use a variety of substrates to degrade, sorb, or precipitate contaminants directly or through microbial activity in the barrier (RTDF, 2006).

5.2.1 Case Study: Nickel Rim Mine Permeable Reactive Barrier

Site History
The Nickel Rim mine site near Sudbury, Ontario, Canada contains a mine tailings impoundment from an abandoned nickel-copper mine. This area has a cool, humid climate, with a mean annual temperature of 4° C and 875 mm mean annual precipitation (Johnson et al., 2000). The impoundment and treatment area are located in a narrow valley with alluvial soils. The shallow aquifer in this area is bounded on the sides and bottom by bedrock (Benner et al., 2002).

Underground mining at Nickel Rim began in 1928, and continued intermittently through 1958. From 1953 to 1958, one million tons of ore were processed. During this time, tailings were deposited into a 9.4 ha impoundment area. The tailings were composed of 3% sulfur by weight, mostly in the form of pyhrrhotite. After tailings deposition ceased, the water table fell below the tailings surface, oxidizing sulfide minerals in the upper layer of tailings and generating acidity. In the 1970's and 1980's, revegetation, sand fill, liming, and seeding were applied to begin site remediation. (Johnson et al., 2000)

Figure 8. Schematic of Nickel Rim mine tailings site and permeable reactive barrier. Reprinted from Mayer et al. 2006.

A plume of contaminated ground water continues to flow at an average velocity of 16 m/year. Approximately 50% of the tailings leachate discharges to the surface near the tailings dam, while the remainder flows through the aquifer. Acidic surface water infiltrates the aquifer both up- and down-gradient of the barrier. Approximately 160 m from the tailings dam, the ground water discharges to Moose Lake. (Johnson et al., 2000; Figure 8)

Ground water leaching from the tailings contained 200 to 2000 mg/L ferrous iron and 1000 to 4000 mg/L sulfate (Mayer et al.,

2006). The ground water pH was between 5 and 6. When this ground water emerged in Moose Lake, iron oxidation and iron oxide precipitation lowered the surface water pH to less than 3. (Benner et al., 2002)

Technology Application
In 1995, a permeable reactive barrier (PRB) was installed in the aquifer 110 m down-gradient of Nickel Rim tailings. The Nickel Rim PRB is 20 m wide and 3.5 m deep, abutting bedrock at its base and sides. The reactive layer is 4 m thick, sandwiched between layers of sand approximately 1 m thick (Figure 8). The reactive layer contains 20% (by volume) municipal compost, 20% leaf mulch, 9% woodchips, 50% gravel, and 1% limestone. A clay cap 30 cm thick covers the top of the PRB. (Benner et al., 1999) The barrier has a hydraulic gradient of 0.016, lower than the surrounding aquifer's hydraulic conductivity of 0.02. Ground water flows through the barrier at an average velocity of 16 meters per year (Benner et al., 2002)

Ground water flowing through the PRB included both deep flow from the tailings impoundment and highly acidic water that infiltrated from the surface (Figure 8; Benner et al., 1999). This accounts for the large variation in water chemistry along the flow path and in the vertical profile. Acidic surface water also recharges the aquifer down-gradient of the PRB, resulting in a shallow untreated layer of water (Benner et al., 1999). Concentrations within the PRB, rather than down-gradient, are reported here to reflect PRB performance.

Construction of the PRB cost $30,000 (RTDF, 2000).

Results
The PRB supported a population of sulfate-reducing bacteria four orders of magnitude higher than those found at any point up gradient. Vertically-averaged influent sulfate concentrations ranged from 2500 to 5200 mg/L in the up-gradient zone, and averaged 840 mg/L within the PRB. Iron removal rates followed trends in sulfate removal, with an efficiency of 68 to 95%. Aluminum, copper, nickel, and zinc all decreased within the sand layer, probably due to increased pH from calcite dissolution or reaction with sediments. No additional removal of these metals was observed within the PRB. (Table 9; Benner et al., 1999)

Table 9. Depth-integrated concentrations at Nickel Rim PRB, 1995-1997.

Analyte	Upgradient	Within PRB
pH	2.8-5.9	6.7
Al	130	<1.0
Cu	3.0	<0.01
Fe	250-1350	80
Ni	0.12-30	<0.1
Zn	1.0	<0.015
sulfate	2500-5200	840
Alkalinity	<1 - 60	2300
SRB numbers (MPN)	2.3 E +2	9.1 E +7

Data from Benner et al., 1999; All concentrations in mg/L

Iron and sulfate were removed by sulfide formation and metal sulfide precipitation, primarily as mackinawite. (Benner et al., 2002) The mass accumulation in the barrier was less than 0.2% of the volume during three years, resulting in fairly constant porosity and permeability of the PRB (Mayer et al., 2006).

On average, ground water had a 90 day residence time in the barrier. The actual residence time ranged from 60 days at the center to 165 days at the edges, due to a ground water flow approximately three times greater in the center of the barrier. Higher sulfate and iron removal rates were also observed at the top and bottom of the barrier, an indication that greater residence time created zones of higher removal efficiency. SRB populations and activity (measured as dehydrogenase activity) were higher in faster flowing zones with higher sulfate concentrations, suggesting the bacteria were responding to chemical concentrations rather than controlling them. Iron removal may not have been maximized because all iron was precipitated in low-flow zones, and excess sulfide was transported out of the barrier without forming metal precipitates. In high-flow zones, precipitation rates may have been a limiting factor that prevented optimum performance from being achieved. (Benner et al., 2002)

The PRB also exhibited seasonal variation in performance. Sulfate and iron removal rates and alkalinity generation were higher in fall than in spring. This pattern was likely related to seasonal variation in temperature within the barrier, especially near the surface. Throughout a three-year study period, the temperature ranged from 2 to 29° C one meter below the surface. This variation is relevant to PRB effectiveness, since bacterially-mediated reaction rates generally double with each 10° C increase. Since the water table of the unconfined aquifer was at or near the ground surface, there was little insulation of ground water from air temperature fluctuations. Temperature change varied much less in deeper regions, with a range of only 7° C at 3.6 m below the surface. (Benner et al. 2002)

A third trend was decreasing effectiveness over time. Sulfate reduction rates decreased 30% and iron removal rates decreased 50% in the first three years of operation. The slowing of sulfate reduction rates occurred most rapidly in the first three months of operation, and at a slower rate over the next 2 years. This pattern is typical of a model in which organic matter of highest reactivity is preferentially consumed, lowering the overall reaction rate. (Benner et al., 2002)

These data were used to produce a process-based reactive transport model, to simulate processes occurring within the PRB. High correspondence between observed and simulated pore water and solid phase chemistry indicated that the conceptual model accounted for important processes. Seasonal and spatial temperature variation, low-flow zones, rapid depletion of labile organic carbon, mackinawite precipitation, and siderite formation were all modeled as important processes. Sulfide reactions with minerals down-gradient, gypsum formation, variation in organic carbon density, and specific mechanisms of organic carbon degradation were not modeled, and may further explain observed changes. (Mayer et al., 2006)

Lessons Learned
- Variable flow is likely to exist in a permeable reactive barrier, and is likely to be a problem. Spatial variation may be minimized by using a more homogenous substrate

mixture, increasing the proportion of gravel, or changing the organic matter particle size distribution.

- To the extent that variable flow can not be easily or economically avoided, thicker barriers or more frequent replacement of reactive materials can be planned, taking into account zones of lower reactivity.

- Temperature variation, both with space and time, can also lead to patchy removal capability. In an aquifer that is closely connected to the surface, where ground water temperature is higher than air temperature, an insulating layer can increase the uniformity and overall efficiency of the PRB. A thicker barrier can also minimize the effects of temperature fluctuations.

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5.2.2 Case Study: Success Mine and Mill Permeable Reactive Barrier

Site History
The Coeur d'Alene River Basin has historically been a rich source of silver, lead, zinc, and other metals. Since the late 1800's, approximately 130 million tonnes of ore have been mined and processed in the area. The Bunker Hill Mining and Smelting Complex in Northern Idaho was the largest of the many mining operations, and housed the largest smelter of its time. (NRC, 2005)

Today Bunker Hill and most other mines are closed and processing has largely ceased, but contamination from tailings and AMD remain. Bunker Hill Mining and Metallurgical Complex, comprised of a 54 km^2 (21 mi^2) area (The Box), was listed as a Superfund site in 1983. Records of Decision were issued in 1991 and 1992 for two Operable Units within the site. In 1998, the EPA began to use its Superfund remedial authority in contaminated areas of the Coeur d'Alene Basin (The Basin) outside The Box, leading to the creation of another Operable Unit covering these areas. (NRC, 2005)

Success Mine and Mill is one site in The Basin that contributes to the AMD problem. The site is in Shoshone County, Idaho, about 8 km northeast of Wallace. This area of Idaho has a mean annual temperature of 5.7° C, and the stream basin receives 1270 mm precipitation per year (NOAA, 2002; Conca and Wright, 2006). The 4 ha site is located on the East Fork of Nine Mile Creek (EFNMC), a tributary to the South Fork of the Coeur d'Alene River. Though the creek is relatively small, its high metal concentrations contribute to the degradation of the Coeur d'Alene. One source of contaminants to EFNMC is a 300,000 m^3 tailings and waste-rock pile, which leaches contaminated water into a shallow aquifer that discharges to the creek. The aquifer is approximately 5 to 6.8 m deep, and composed of alluvial materials mixed with some tailings. Ground water flows through the aquifer between the tailings and the stream range from 11 to 370 L/min (3 to 100 gpm), with strong seasonal precipitation effects. (Conca and Wright, 2006) Soil concentrations of lead, zinc, and cadmium were as high as 1,000 to 4,000 mg/kg prior to treatment. Ground water contained up to 1.44 mg/L lead, 177.0 mg/L zinc, and 1.25 mg/L cadmium. The average pH of the ground water was 4.5. (Adams et al., 2006)

Prior response actions at the site included relocating the EFNMC to an armored channel, constructing a berm between the tailings pile and the creek, and diverting surface water away from the pile (Conca and Wright, 2006). A team of federal, state, local and tribal officials, mining company representatives, and consultants ultimately chose to install a permeable reactive barrier to provide continuous treatment at the site (Conca and Wright, 2006). The full-scale field test was intended to provide information on the feasibility of using passive treatment barriers to treat ground water, one of the preferred options in the Record of Decision for The Basin. It has also been used to evaluate the suitability of different reactive media within PRBs. (Stromberg and Yancey, 2004)

Technology Application
The Success Mine and Mill PRB was constructed in 2001. The barrier was built in a trench approximately 4.5 m wide, 4.1 m deep, and 15.2 m long, between the tailings deposit and the EFNMC, with the long axis parallel to ground-water flow. The trench was lined and divided into two parallel cells by Portland cement. Plywood baffles subdivided each cell into a series of five

chambers, causing flow to change directions within the barrier (Figure 9). Internal plumbing and valves allowed sampling and replacement of reactive material. (Adams et al., 2006) The PRB was covered with steel plates, with access openings for the intake and outflow ports (Conca and Wright, 2006).
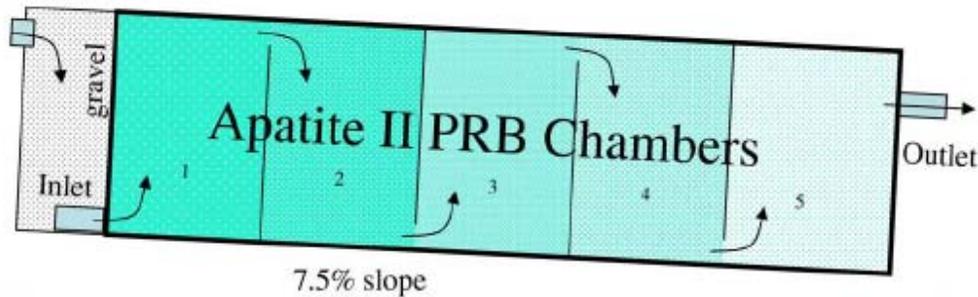

Figure 9. Schematic cross-section of Success Mine PRB. Reprinted from Conca and Wright, 2006.

A 441 m containment wall extending down to the bedrock was installed to direct ground water to the PRB. A hydraulic drain directed water that collected in the aquifer upgradient of the PRB into the barrier's intake. The vault contained one inflow port and two outflow ports, with a head difference of 2.3 m across the barrier (Conca and Wright, 2006). The design flow of the system was 19 L/min (5 gpm), yielding a residence time of 24 hours within the PRB. (Adams et al. 2006).

The reactive material selected for this trial of the PRB was Apatite II™, a technology of PIMS NW, Inc. Apatite II is a metal stabilization substrate made from processed fish bones, which serves as source of phosphorus, carbon, buffering, and surface sorption sites. It can provide both organic carbon and electrons for bacterially-mediated sulfate reduction. The barrier was filled with 90 tonnes of Apatite II. (Conca and Wright, 2006).

The cost of construction of the barrier was approximately $500,000 (Adams et al., 2006). Since construction, additional Apatite II was purchased at $350 per ton for media replacement, with a total cost of $100,000 to date. Excluding media replacement, maintenance costs have been $10,000 over three years, mainly for air injection (N. Yancey, pers. comm., 2006).

Results
The PRB reduced concentrations of the three target metals in ground water by 99%. Effluent concentrations of cadmium and lead were generally below detection limits. After passing through the barrier, pH increased to 6.5-7.0 and sulfate concentrations were decreased from 250 mg/L to 35-150 mg/L. (Adams et al., 2006) Data characteristic of concentrations from 2001 to 2004 are presented in Table 10.

Table 10. Success Mine PRB water chemistry, 2003

Analyte	Influent	Effluent	Criteria
pH	4.18	7.13	6.5-8.5
Cd	0.42	<0.001	0.005
Pb	1.16	<0.001	0.015
Zn	64.5	0.086	5
Sulfate	216	68.2	250

Data from Conca and Wright, 2006; All concentrations in mg/L

The sulfate and metal removal rates, redox potential (-100 to -300 mV), alkalinity increase, and solids formed in the barrier are consistent with the mechanism of sulfate reduction and metal sulfide precipitation. Evidence of this pathway is particularly strong for zinc, as sphalerite (ZnS) was one of the primary metal solids found in the barrier. Dissolution of Apatite II and precipitation of solids such as pyromorphite $[Pb_{10}(PO_4)_6(OH)_2]$ is a likely mechanism for lead removal, based on the presence of this solid. Sorption and co-precipitation are two other mechanisms that may account for additional metals removal. (Conca and Wright, 2006)

Flow variation
The pilot PRB typically received about 11 L/min inflow, but received up to 190 L/min during runoff events. This variability caused overflows during high-flow periods and exceeded the system's treatment capacity. (Stromberg and Yancey, 2004) Seasonal fluctuation of flow is also problematic because high flows alter the barrier material, which then gets compacted during low-flow periods, forming preferential flow paths (N. Yancey, pers. comm., 2006). Therefore, design changes or maintenance are needed to address flow fluctuation.

Clogging and channel formation in the reactive material were especially persistent in the East Cell of the barrier. Silica buildup in the intakes and decomposition of apatite reduced flow from 114 L/min to 19 L/min. In 2002, the intakes were reconfigured and substrate in the East Cell was replaced with a 50% gravel: 50% apatite mixture. (Adams et al., 2006) Replacing the media increased flow for only six months, after which flow through the East Cell gradually declined over three years. Though the barrier was designed for a flow rate of 19 L/min (5 gpm), it was desirable to reduce the amount of drainage bypassing the barrier, to minimize the introduction of untreated AMD to the EFNMC. (N Yancey, pers. comm., 2006)

In the spring of 2005, compressed air was injected through the reactive media of both cells, restoring flow by disturbing and redistributing the apatite (Stromberg and Yancey, 2004). This resulted in a temporary increase in flow through the PRB, and reduction of overflow around it. Air sparging once a year is expected to be effective in maintaining flow through the barrier (N. Yancey, pers. comm., 2006).

The third, and most recent, flow restoration technique was replacing the reactive media in the East Cell with a mixture of 70% (by volume) Apatite II and 30% plastic packing rings in fall of 2005. This material yielded higher flow than the West Cell, a rate that has been maintained through June 2006, the most recent sampling date. If such results persist, the need for air injection could be reduced or eliminated. (N. Yancey, pers. comm., 2006)

Other concerns
The use of phosphorus-rich apatite substrate may increase effluent phosphate concentrations. Total phosphate concentrations typically increased through the barrier, though they usually remain below 10 mg/L (Conca and Wright, 2006). Potentially high phosphate concentrations make it desirable to monitor loadings of this and other nutrients.

After four years of operation, the barrier was estimated to be approximately 40% spent. As mentioned above, the apatite-gravel mix was removed from one cell and replaced with a mixture of apatite and plastic packing rings. The spent reactive material was found to be non-hazardous and disposed of on-site. (Adams et al. 2006) The West Cell continues to function after six years. Since over 80% of the metal removal occurred in the first two chambers of each cell, only part of the media would need to be replaced in a properly functioning cell to extend its lifetime (Conca and Wright, 2006).

Lessons Learned
- A permeable barrier with Apatite II reactive media is capable of supporting SRB-mediated metals removal.
- Substrate changes can lead to plugging or channeling in the barrier. Air injection can temporarily resolve this problem.
- Alternative mixes of media are being tested to alleviate flow problems. A 7:3 mixture of packing rings and apatite has improved flow.
- Reactive media will likely need to be replaced in 10 to 15 years, especially for up-gradient portions.

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5.3 Pit Lake Treatment

5.3.1 Case Study: Anchor Hill Pit Lake Bioremediation

Site History
Gilt Edge Mine is located 8 km east of Lead in the Black Hills of South Dakota. Gold, copper and tungsten have been mined in this area since the 1870's. From 1987 to 1999, Brohm Mining Company operated a 667 ha open pit gold mine in sulfidic, acid-generating rock. The operation included three open pits, a cyanide heap leach pad, and a 9 million cubic meters (12 million yd^3) waste rock dump. Brohm Mining became insolvent and was unable to maintain treatment of site impacts by 1999, leaving behind 568 million L (150 million gallons) of AMD, as well as solid wastes with further acid-generating capacity. (US EPA, 2006)

The South Dakota Department of Environment and Natural Resources took over water treatment until August 2000, when it turned treatment over to the U.S. EPA. The site was proposed for the Superfund National Priorities List in May 2000, and listed in December 2000. Emergency response and interim clean-up activities have included interim water treatment operations using an upgraded active treatment plant, and work on regrading and capping the Ruby Gulch Waste Rock Repository. Treatability tests, including bioremediation of Anchor Hill Pit Lake, are ongoing. (US EPA, 2006)

Contamination at the site threatened cold-water fisheries and municipal water supplies downstream. Mine drainage contained high concentrations of arsenic, cadmium, cobalt, copper, lead, zinc, nitrates, and sulfates. Copper, cadmium, and zinc releases to Strawberry and Bear Butte Creeks appeared to present the greatest environmental risks. (US EPA, 2006)

The Bioremediation of Anchor Hill Pit Lake was developed collaboratively by EPA Office of Research and Development, the Mine Waste Technology Program (Activity III, Project 34), and EPA Region VIII. The purposes of this project were to evaluate the potential for passive bioremediation of pit lakes in general, and to examine the feasibility of using pit lake treatment as a final remedial action at Gilt Edge Mine. A potential application of this treatment at Gilt Edge would be to collect AMD from throughout the site, treat it within the pit lake, and discharge the water into Strawberry Creek. (Harrington et al., 2004)

Anchor Hill Pit Lake contained 273 million liters (72 million gallons) of acid rock drainage. The pit lake has a maximum depth of 26 m. The water in the lake originally had a pH of approximately 3 and had metals, nitrate, and sulfate concentrations in excess of State water quality standards (Table 11). The goal of this treatment was to reduce these concentrations to levels meeting South Dakota Ambient Water Quality Criteria, allowing treated water to be discharged to surface water. (Harrington et al., 2004)

Technology Application
The Anchor Hill Pit Lake treatment involved two phases:
1. Lake neutralization using NeutraMill® lime treatment
2. Biological nitrate, sulfate and metals removal via Redox-Mediated Biotransformation (RMB™) technology patented by Green World Science ® and owned by ARCADIS G&M

From March to May 2001, 265 tonnes of powdered lime was dispensed and mixed into the pit lake at a rate of 1.4 tonnes/hour, using a NeutralMill device (Harrington et al., 2004). The pH stabilized near neutral in May 2001, then dropped to approximately 4.5 by the end of that month. To further neutralize the lake, 43,630 kg of 50% sodium hydroxide solution was added in April 2002, and again in September 2002 (Table 11; Park, 2006). Neutralization was complete in fall 2002. The original neutralization was incomplete due to incomplete operation of the NeutraMill, lower lime utilization efficiency than expected, and acidic spring runoff (Harrington et al., 2004).

Deployment of RMB technology began in May 2001. Organic matter was added on four dates, to stimulate microbial activity. A total of 243,700 kg molasses and 76,730 kg methanol were added by truckload; therefore, all quantities are approximate (Table 11; Park, 2006). Wood chips were also added for bacterial attachment sites. Relatively small amounts (less than 2,300 kg) of phosphoric acid were added as a phosphorous source for algae, but were probably consumed by later alkalinity additions (Harrington et al., 2004).

Table 11. Additions to Anchor Hill Pit Lake, 2001-2003

Date	Alkalinity		Organic matter	
Mar-May, 2001	lime	265,000 kg		
May, 2001			molasses	130,900 kg
			methanol	31,640 kg
Oct, 2001			molasses	45,130 kg
			methanol	22,490 kg
April, 2002	50% NaOH	43,630 kg	molasses	22,870 kg
Sept, 2002	50% NaOH	43,640 kg	molasses	44,800 kg
			methanol	22,600 kg

Data from Park, 2006

The in-lake treatment was monitored at two buoys located one-third and two-thirds the length of the lake. Water samples at two depths, sediment samples, and vertical profiles of physical characteristics were taken at each sample point. This project was monitored through early 2006, and a final report with further details on this project will be available at the end of the year from EPA ORD. (Park, 2006)

Results

Acid neutralization and carbon addition promoted microbial activity in Anchor Hill Pit Lake, leading to reductive removal of contaminants of concern. By late 2002, reducing conditions existed in the lake. As redox potential decreased, various chemical constituents in the lake successively served as electron acceptors for microbially-mediated organic carbon oxidation. After dissolved oxygen was depleted (by June 2001), nitrate was gradually consumed through denitrification (by March 2003). As nitrate availability decreased, iron (III) reduction occurred (2002 to 2003), which initially increased dissolved iron (II) concentrations. Sulfate was presumably the dominant electron acceptor by late spring 2003, based on the presence of sulfide in the lake, dissolved metals removal, and the low redox potential. (Harrington et al. 2004)

With the onset of sulfate reduction, dissolved copper, cadmium and zinc concentrations decreased more rapidly. By the end of 2003, a 99% reduction in these three target metals was observed and all other metals of concern met South Dakota water quality standards. Total metals concentrations also fell below water quality limits in the following years (Table 12). Though selenium concentrations were not detectable in samples from 2003 and 2004, they later increased to approximately 0.015 mg/L, which was higher than the acute and chronic ambient water quality criteria (Park, 2006).

Table 12. Anchor Hill Pit Lake water chemistry, before and after treatment.

Analyte	Dissolved concentration				Criteria	
	Pre-treatment, March 2001	Post-neutralization, Oct. 2001	Post-treatment, Oct. 2003	Post-treatment, Sept. 2004	Chronic	Acute
pH	3.3	5.07	7.08	--	>6.5	--
Al	223.5	44.2	--	<5	--	--
As	0.073	0.0016	bdl	--	0.19	0.36
Cd	0.576	0.28	0.0028	<0.00035	0.003	0.017
Cu	43.3	13.2	0.0218	<0.00048	0.037	0.063
Fe	15.7	0.127	--	<0.5	--	--
Se	0.026	0.0203	bdl	<0.004	0.005	0.02
Zn	14.1	6.55	0.103	0.04	0.338	0.37
NO$_3$-N	82.9	47.8	bdl	--	50	88

Data from Harrington, 2004 and Park, 2006; all concentrations in mg/L
bdl=below detection limit; -- = not reported

As expected, sulfate-reducing bacteria did not reach maximum activity levels until oxidized nitrogen compounds were nearly exhausted. Because denitrification yields approximately 42% more energy per mole of carbon oxidized, denitrifying bacteria outcompete SRB when sufficient nitrate is available. Also, oxidized nitrogen-containing compounds can re-oxidize sulfide produced in reducing microenvironments, counteracting the effects of SRB. (Harrington et al. 2004) Therefore, excessive nitrate addition is not desirable in using SRB treatment for metals removal.

The pit lake additions altered turnover patterns of the lake. Anchor Hill Pit Lake became chemically stratified in fall 2001, and ceased mixing. This condition was maintained and strengthened as the treatment progressed. Melting ice, spring runoff, and precipitate settling from the surface water have all reinforced the development of a chemical and density gradient in the water column. (Harrington et al. 2004) The pit lake currently has three zones: a well-mixed surface zone of 3 m, a chemocline with gradually increasing conductivity from 3 to 12 m, and a relatively uniform layer below 12 m that is isolated from the surface (Park, 2006).

Discharging pit lake water
To accomplish one goal for this project, the potential for discharging pit lake water into Strawberry Creek was tested. Some water quality concerns necessitated additional treatment of pit lake water prior to discharge. Specific conductivity, total dissolved solids, total suspended solids (TSS), BOD, and hydrogen sulfide were all higher than regulatory standards allowed. The

dissolved oxygen was also too low to permit discharge of the water without further treatment. (Park, 2006)

In June 2004, a discharge of 568,000 L (150,000 gallons) was pumped from the bottom layer (15 m below the surface) in batches of increasing volume. Reduced, deeper water was extracted to avoid disturbing the stratification of the lake, and potentially releasing accumulated hydrogen sulfide. The water was filtered due to total suspended solids and total metals. Filtration through 25 μm and 1 μm bag filters was only partially successful. Tests found that a 0.45 μm filter would be required for effective filtration. To meet BOD, undisassociated hydrogen sulfide, and dissolved oxygen requirements, the water was pumped into an aeration pond, where it was aerated with a sprinkler system. Because hydrogen sulfide gas releases were a health and safety concern, this process was monitored and conducted under appropriate wind conditions. Much of the abundant sulfide in the water was oxidized to elemental sulfur, greatly increasing the turbidity and TSS. After the solids settled, the water was dischargeable. A later batch test used modified mining equipment to rapidly aerate water and remove hydrogen sulfide, speeding up the aeration process, but not the settling time. (Park, 2006)

Due to the cost and difficulty of discharging deep pit lake water, the viability of surface water discharge was tested. An evaluation of the likelihood of mixing (Lake and Wedderburn numbers) determined that lake turnover was improbable under foreseeable wind conditions. Water withdrawn from the surface layer met all discharge criteria, except specific conductivity, total dissolved solids, and dissolved selenium. Waivers were granted for these parameters. Water was discharged at a rate of 1325L/min (350 gpm), using a perforated pipe system (Figure 10). A total of 114 million liters (30 million gallons) have been discharged, without detriment to pit lake treatment or the receiving stream. (Park, 2006)
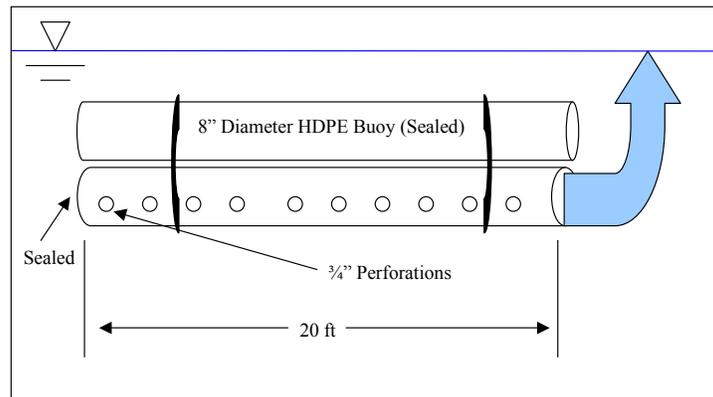

Figure 130. Configuration of water withdrawal device.

As the persistence of excess dissolved hydrogen sulfide below the chemocline was a health and safety concern, a decision was made to eliminate it prior to project completion. Ferrous iron salts, ferric iron salts, and hydrogen peroxide were all effective in bench tests. Oxidation with hydrogen peroxide was selected as the most cost-effective treatment. A total of 14,800 L (3,900 gallons) of 50% hydrogen peroxide were added in three locations over two days. Water column mixing was sufficient to remove most hydrogen sulfide in four months, with the exception of a 15 mg/L spike at the 18-meter depth. (Park, 2006)

The Anchor Hill Pit Lake treatment is essentially complete. Additional pit water may be discharged, as feasible. Treatment of other ARD sources on the site has been considered, but no plans are in place for additional water treatment (Park, 2006).

Lessons Learned
- Passive, in-lake treatment using lime neutralization and redox-mediated biotransformation shows promise for treating AMD.
- Effectively mixing lime and other alkaline agents into large pit lakes is a challenge to neutralization efforts.
- Significant time (over a year) may be required for neutral, reducing conditions to develop, and SRB activity may be further delayed by the availability of other reductants such as nitrate.
- Adding excess carbon may lead to more sulfide production than required to precipitate metals, resulting in hydrogen sulfide accumulation.
- "Batch" treatment and discharge of pit lake water to surface water appear feasible. Additional work is needed to control hydrogen sulfide releases, remove colloidal precipitates, and investigate continuous treatment methods.

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5.4 Technology in development

5.4.1 In Situ Reactive Layers

Sulfate-reducing bacteria are involved in some *in situ*, source control measures. Like the Lilly/Orphan Boy bioreactor and Anchor Hill Pit Lake, various methods of treating AMD or acid-generating material in place are being investigated. Bioremediation has been employed by inducing SRB activity at the source: mine tailings, mine workings, or contaminated soil. The field study at Kidd Creek Metallurgical site is one example of amendment addition to promote SRB activity and prevent acid mine drainage.

Site History
The Kidd Creek Metallurgical Site near Timmins, Ontario is an active metal mine where tailings have been deposited in a 1200 ha impoundment. The tailings contain high percentages of pyrite and pyrrhotite, as well as carbonate minerals. Because the water table is below the surface, the tailings have become oxidized, releasing sulfate, iron oxyhydroxides, and acidity. Water flows in near the center of the tailings impoundment, and is discharged at the edge of the impoundment at a velocity of approximately 0.1 m/year.

Treatment
Reactive treatment layers were created in August 1999, to test the ability of different organic amendments to induce sulfate reduction. Three test cells were made from vertical sheet piling. The cells were 2.7 m wide, 3.4 m long and 2 m high, and were left open at the top and bottom, so ground water could flow through the tailings. In each cell, the top meter of tailings was excavated. The tailings were replaced with a well-mixed slurry of tailings and organic matter (4:1 by volume) in two of the cells, and by tailings only in the control cell. One organic carbon treatment consisted of woodchips; the other was pulp waste.

Pore water was sampled with piezometers at half-meter intervals. Microbial analysis was completed using soil cores taken at five locations within each cell. While SRB growth would be optimal in the absence of oxygen, as occurs in saturated mine tailings, the Kidd Creek tailings were unsaturated in the upper 0.2 m, tension-saturated from 0.2 to 0.6 m, and saturated below this depth. Consistent with the chemistry of oxidized tailings, the top 0.2 m of tailings had low pH, and high concentrations of sulfate and metals before amendment addition. The mixing process increased concentrations of metals (Fe, Mg, Mn, Na, Ni, Si, Zn) and sulfate, relative to undisturbed tailings. The pH and alkalinity were slightly higher in mixed tailings, probably due to neutralization reactions with carbonate minerals.

Results
The woodchip-amended cell had a sulfate reduction rate of 500mg/L per year, corresponding to a decrease in redox potential from 70 to 0 mV over the year. Zinc concentrations decreased by up to 400 mg/L. No change in iron concentration was observed, probably because the lower solubility of FeS causes it to precipitate after ZnS. Sulfate-reducing bacteria populations were highest at 1.2 m depth, and were higher than the control below this depth. Slightly lower concentrations of iron, zinc, and sulfate were also observed in the woodchip-amended cell at this depth. Microbial populations suggested that the woodchip amendments may actually have been

mixed into tailings as deep as 1.2 m below the surface, rather than the intended mixing depth of 1 m.

The pulp-amended cell had a much higher sulfate reduction rate of 5,000 mg/L per year. The greatest change was observed at the interface of the amended and unamended zones, where sulfate concentrations were 65 to 70% lower, iron concentrations were 80 to 99.5% lower, and zinc concentrations were over 99% lower than the unamended tailings. Alkalinity ranged from 113 to 319 mg/L at the interface, while it was 75 mg/L at the same depth in the unamended cell. In the upper meter of tailings, sulfate, iron, and zinc concentrations were lower in the amended cell than in the unamended tailings, though the difference was less pronounced. As the geochemical properties suggest, SRB populations were highest at the amended-unamended interface, and lower in the unsaturated zone. Overall, SRB numbers were one to two orders of magnitude higher than the control.

Lessons learned
- Pulp waste is a more effective organic carbon source than woodchips in promoting SRB-mediated treatment of mine tailings, though both stimulated some sulfate reduction.
- SRB activity is concentrated at amendment interfaces, in saturated zones, and in zones of high sulfate and carbon availability.
- Alkalinity increase due to sulfate reduction may not be fully reflected in water chemistry, due to subsequent removal in precipitation reactions.

Project Reference:
Hulshof, A.H.M., D.W. Blowes and W.D. Gould, 2006. Evaluation of in situ layers for treatment of acid mine drainage: A field comparison. Water Research 40:1816-1826.

5.4.2 Modular Sulfate-Reducing Bioreactor Design

Based on field and laboratory studies, the Mine Waste Technology Program (Activity III, Project 24) has designed a modular sulfate-reducing bioreactor constructed in a tank, or Reactive Cartridge (RC). To assist in designing appropriate bioreactors for the AMD to be treated, MWTP has also developed the computer program *Bioreactor Economics, Size and Time of operation* (BEST).

The RC design emerged from the need for treatment systems that allow transportation of materials to remote sites and replacement of bioreactor substrate to maintain functionality. Like a typical sulfate-reducing bioreactor, the RC is designed to provide high permeability, an organic carbon supply, anaerobic conditions, and ability to accumulate precipitated metals.

While carbon source selection depends on cost, availability of materials, and AMD characteristics, a mixture of cow manure and walnut shells is used as a sample substrate. A quickly degradable substance like cow manure provides:
- potential for quick startup
- nitrogen for decomposers
- moderate total organic carbon

A recalcitrant carbon source like walnut shells provides:
- long-term carbon supply
- structural support that resists compaction
- a matrix to keep manure evenly distributed
- high total organic carbon
- high surface area to maximize AMD contact with substrate

A mixture of 20% manure and 80% walnut shells was found to be an effective proportion in prior experiments. This mixture has a hydraulic conductivity of approximately 0.01 cm/s.

The bioreactor system design allows multiple RC to be arranged in parallel or in series, as appropriate to the flow rate, acidity, and metal concentrations of the AMD. The original RC design is an 8-foot-tall, 8-foot-diameter HDPE or polypropylene tank (2,500 gallon volume), filled with five-gallon plastic mesh bags containing the substrate mixture. Key design features include:
- placing inlet and outlet pipes near top of tank to retain settled materials
- 4-inch vertical perforated pipes for AMD distribution and bioreactor cleaning
- 10-inch vertical outlet pipe to remove precipitates with a suction pump
- A layer of high-conductivity substrate (walnut shells) around distribution pipes
- A layer of low-conductivity substrate (manure) around outlet pipe
- Plastic tarp covered with substrate bags and removable tank lid to maintain anaerobic conditions
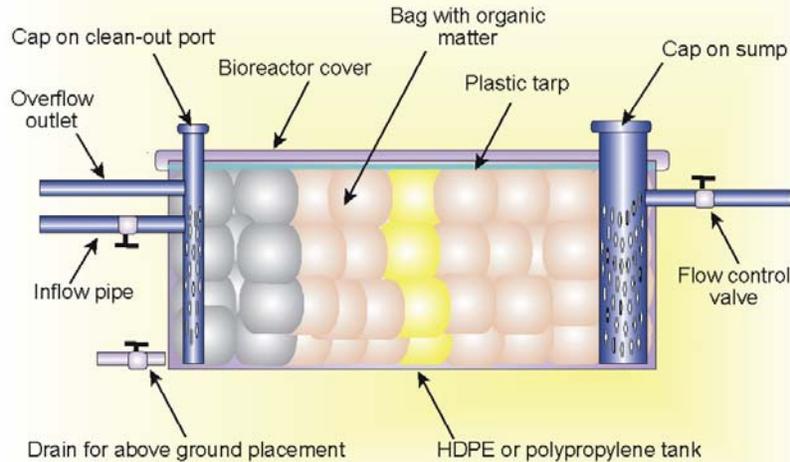
Figure 11. Conceptual cross-section of reactive cartridge. Reprinted from MSE, 2006.

The size of this modular system allows the prefabricated tanks to be transported to the site on a flatbed truck, with minimal operation on-site, which is important for remote sites without power. Construction of the RC bioreactor occurs in three main steps: installing the tanks and pipes, lowering bags into the tank in layers, and saturating each layer with AMD before placement of the next layer.

The BEST computer simulator uses spreadsheet calculations to calculate design and cost parameters. The BEST model is intended to receive geochemical information from the public domain software PHREEQCI (USGS, 2002). PHREEQCI is an interactive graphical user interface for the PHREEQC (pH, redox, equilibrium) geochemical computer model (Parkhurst and Appelo, 1999). BEST is a model in the form of a Microsoft Excel™ workbook with 17 worksheets, many of which are linked. The simulator can be run for systems that remove metals only through metal sulfide precipitation or for systems that remove metals by precipitation as sulfides and hydroxides. The BEST simulator can be used to estimate the quantity of organic carbon required to precipitate metals in the AMD, the number of RC needed, the sulfate reduction rate and associated carbon use, the hydraulic residence time, the amount of materials and labor required, construction and operation costs, and net present value. The information needed to run the combined PHREEQCI/BEST simulation includes the chemical properties and flow rate of AMD, the substrate type and TOC content, unit costs of materials and labor, experimental data on the sulfate reduction rate for the substrate chosen, and the discount rate. Default values for some parameters, such as sulfate reduction rate for the substrate, are provided.

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Unless specified, all information is from:
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Other references cited :
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U.S. Geological Survey (USGS), 2002. PHREEQCI—A Graphical User Interface to the Geochemical Model PHREEQC. U.S. Geological Survey Fact Sheet FS-031-02.

6. CONCLUSIONS

SRB capabilities

1. Anaerobic systems utilizing sulfate-reducing bacteria have successfully reduced sulfate, removed metals with up to almost 100% efficiency, and produced alkalinity to treat acid mine drainage (see table A-1).
2. Alkalinity addition, generally in the form of limestone, and occasionally sodium hydroxide, enhanced the activity of SRB. Though bacteria have been found to survive at pH 2.5, increasing the pH to at least 4.0 yielded better performance. Most metal precipitation was more efficient at a higher pH.
3. Low temperatures generally reduced SRB activity. SRB activity doubled for each 10° C increase in a PRB study. Installing biological components below grade, covering reactors with insulating material, or controlling winter inflows can minimize temperature effects. Sub-freezing ambient temperatures did not preclude effective treatment in the bioremediation systems examined.
4. Sulfate-reducing bacteria sources may affect success of treatment, especially in very acidic conditions. Inoculating systems with tolerant SRB previously exposed to AMD, or developing diverse, tolerant microbial communities through gradual exposure may improve treatment.
5. Introducing excessive oxidized iron solids into bioreactors may negatively impact treatment systems. Positioning aerobic cells down-gradient of bioreactors and allowing solids to settle out of bioreactor influent can help prevent this.
6. Depletion of organic carbon in bioreactors creates a tendency for decreased performance with time. Lab and pilot tests of carbon sources, replaceable organic matter cartridges, and continuous liquid carbon source addition are strategies used to address this problem.
7. Manganese was not effectively treated with SRB to precipitate metal sulfides. Passive systems that successfully removed manganese did so by creating suitable conditions for manganese-oxidizing bacteria; proper aeration, excess sulfide removal, and circumneutral pH were important factors in its removal.

Engineering concerns

8. Seasonally high flows commonly reduced system performance or caused overflow of untreated water. This was remedied in some systems by having extra storage or treatment capacity. Diverting clean water away from the system may prevent overloading.
9. Flow problems (hydraulic conductivity loss or preferential flow paths) are pervasive in wetland, bioreactor, and PRB systems, due to precipitate build-up and substrate settling. Flushing systems, air injection, replacing reactive material, and using 70-100% non-degradable matrix materials have all been employed to restore flow.
10. Recirculation can be used to moderate AMD acidity, increase treatment efficiency, and prevent clogging.
11. Treatment effectiveness varies spatially, with flow variability, temperature gradients, and organic substrate variability. Increasing substrate uniformity can enhance performance uniformity and possibly overall success. Spatial variability is also an important consideration in monitoring protocol.

12. High biochemical oxygen demand can pose water quality concerns when SRB-treated water is discharged. Many systems utilize an aerobic polishing pond or a rock-lined channel to retain organic matter and reoxygenate the effluent. Nitrogen- and phosphorus-containing substrate may also elevate effluent concentrations and should be monitored and addressed if necessary.

13. Bench-scale and pilot-scale tests are important information sources for the design of most types of treatment system.

14. There appeared to be a trade-off between maintenance requirements and system performance. A truly passive system may be possible for small or less toxic AMD sources, but variation or high loading make maintenance necessary within the first decade of operation. Though all systems required less effort than daily operation of active treatment plants, maintenance requirements varied from weekly to every few years, to maintain performance. As many environmental factors can interfere with treatment, regular monitoring is also important.

15. Treatment system design must incorporate considerations of AMD chemical composition, climate, space, cost, site accessibility, available materials, and discharge standards. Modeling tools for AMD generation and bioreactor design, as well as some general guidelines, can facilitate the effort.

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APPENDIX

A. Case Study Summary Tables

Basic features and performance measures of passive treatment systems included as case studies in this paper are summarized in Appendix Tables A-1 and A-2. Because of the variation in treatment system type, contaminant levels, and goals, average removal rates should not be assumed to apply to all systems. The difficulty of obtaining information on unsuccessful treatments due to termination or lack of reporting should also be noted.

Table A-1. Summary of Case Studies

SiteName	Location	Contaminants	Media	Technology Type	Flow Rate (L/min)	Construction Cost	Operational Period	% removal								pH in	pH out
								Al	Cd	Cu	Fe	Pb	Ni	Zn	Sulfate		
Yellow Creek 2B	Indiana Co., PA	Al, Cu, Fe, Ni, Zn	sw	bioreactor	38	$158,000	2002-present	99.8	--	91.0	98.9	--	99.4	93.0	--	3	6.6
Wheal Jane Tin Mine*	Cornwall, UK	Zn, Cu, Cd, sulfate	sw	integrated bioreactor system	36	$1,700,000 (3 systems)	1997-2002	82.3	88.4	51.0	99.8	--	--	95.9	60.2	3	6
West Fork Mine	Reynolds Co., MO	Pb, Zn	sw	bioreactor	4,540	$700,000	1996-present	--	33.3	78.4	--	91.7	--	37.5	22.2	7.8	7.8
Lilly/Orphan Boy Mine	Elliston, MT	Al, As, Cd, Cu, Fe, Zn, sulfate	sw	*in situ* bioreactor	11	not available	1994-present	94.7	80.6	87.2	-25.1	--	--	52.1	--	3	6
Surething Mine	Elliston, MT	Fe, Al, Cu, Zn, Pb, As, Cd, Mn	sw	integrated bioreactor system	8-11	$250,000	2001-2005	99.9	100.0	99.9	99.9	97.4	--	100.0	59.6	2.6	7.3
Leviathan Mine	Markleeville, CA	Al, Fe, Cu, Ni, Zn	sw	liquid C bioreactor system	22-83	$836,000-$864,000	2003-present	98.3	66.7	99.3	99.0	--	75.4	92.0	16.9	3	7
Nickel Rim	Sudbury, Ontario	Fe, Ni, sulfate	gw, sw	PRB (compost)	not available	$30,000	1995-1998	99.2	--	99.7	>68.0	--	99.7	98.5	73.8	4	6.7
Success Mine and Mill	Shoshone Co., ID	Pb, Zn, Cd	soil, gw	PRB (apatite)	19	$500,000	2001-present	--	99.8	--	--	99.7	--	99.9	40.0	4.5	6.5
Gilt Edge Mine	Deadwood, SD	Cd, Cu, Pb Se, Zn, sulfate, nitrate	gw, sw	pit lake amendment	not applicable	not available	2001-2006	--	99.5	99.9	--	--	94.2	99.3	--	3.3	7.1
							Average	95.7	81.2	88.3	74.5	96.2	92.2	85.3	45.4	3.8	6.8
							Median	98.8	88.4	95.1	99.0	97.4	96.8	95.9	49.8	3.0	6.7

Note: cost and removal data are for entire system; volume is for component(s) supporting SRB

* Chemical results are for lime-free system only

Table A-2. Substrate and SRB source used in studied systems

SiteName	Substrate	Volume (m^3)	SRB Source
Yellow Creek 2B	50% woodchips, 30% limestone, 10% cow manure, 10% hay	988	cow manure
Wheal Jane Tin Mine	95% sawdust, 5% hay	765	cow manure
West Fork Mine	67% sawdust, 19% limestone, 12% manure, 2% alfalfa	6840	pilot system substrate, manure
Lilly/Orphan Boy Mine	cow manure, hay, woodchips	not available	cow manure
Surething Mine	50% cow manure, 50% walnut shells	167	cow manure
Leviathan Mine	river rock, ethanol-fed	235	cow manure
Nickel Rim	20% municipal compost, 20% leaf mulch, 9% woodchips, 50% pea gravel, 1% limestone	216	indigenous
Success Mine and Mill	100% apatiteII or 70% apatiteII, 30% plastic packing rings	280	indigenous
Gilt Edge Mine	molasses, methanol, lime	272,500	indigenous

B. Lessons Learned Summary Tables

Table B-1. Features of delivery systems for SRB treatment

Treatment System Design	Defining Features	Advantages	Problems	Solutions
Anaerobic Constructed Wetlands	• Standing water or wetland vegetation	• Long history of use (coal mines) • Habitat/aesthetic value	• Clogging • Temperature effects • Space requirements • May be toxic to wildlife	• Flushing • Appropriate site selection
Solid Matrix Bioreactors	• Contained pond or cell, often below grade • Not vegetated • Filled with some % organic C	• Easy access for maintenance • Temperature resistance	• Clogging • Loss of C availability	• Flushing • Organic matter replacement
Liquid Carbon Source Bioreactors	• Contained pond or cell, often below grade • Not vegetated • Filled with rock or inactive material • Liquid C source added	• Substrate stability • Consistent C input	• Some clogging • Little history of use • More frequent site visits • Chemical costs & storage • Energy for pumps	• Flush, pump sludge ponds • Recirculate effluent • Remote monitoring • Solar/wind power
Permeable Reactive Barriers	• Intercept ground water flow	• Little above-ground space • Minimum pipes required	• Clogging • Loss of C availability	• Air sparging • Reactive material replacement • Different substrate mixtures
Pit Lake Treatment	• AMD storage in a pit lake • Alkalinity and carbon added	• In situ- pit lakes already exist • Long retention time	• Large amount of inputs at once • Slow startup • Mixing difficulties • H_2S, BOD, TSS, DO problems • Continuous treatment not tried	• Allow to proceed slowly • Time early steps around turnover or explore other mixing devices • Avoid excess C addition • Post-treatment
Organic Amendments	• Organic matter addition to solid mine waste or structures	• AMD prevention • Low-cost • Easily combined with other treatments	• Little history of use (for SRB) • Less control over conditions • Long-term effectiveness unknown	• Monitor • Plan for periodic addition • Combine with other treatments

Table B-2. General advantages and disadvantages of passive treatment with SRB

Advantages	Disadvantages
Low cost	Limited to low flows or concentrations
Fewer site visits	Less control over some parameters
Little or no power required	Require some maintenance or renovation
May utilize waste material	Potentially high space requirement
Effective for multiple contaminants	Less technical experience
Effective in neutral, acidic or alkaline conditions	Potential odor problems
Little sludge generation	Low effectiveness for Mn
Inconspicuous or natural appearance	Need for polishing after treatment
May resist freezing	H_2S Production
Easily combined with other passive treatments	

Table B-3. Potential problems and solutions in SRB treatment systems

Problems	Solutions
Clogging/channelization	Porous, nondegradable material; flushing
Seasonally high flows	Storage; diversion
Carbon source depletion	Replacement; excess C; mixture of materials
Low pH stresses SRB	Acidophilic species; alkalinity addition; recirculation
Low temperature	Below-ground installation; impermeable covers
Little or no Mn removal	Add aerobic rock filter
High BOD, solids; low DO	Aeration/polishing pond or rock filter