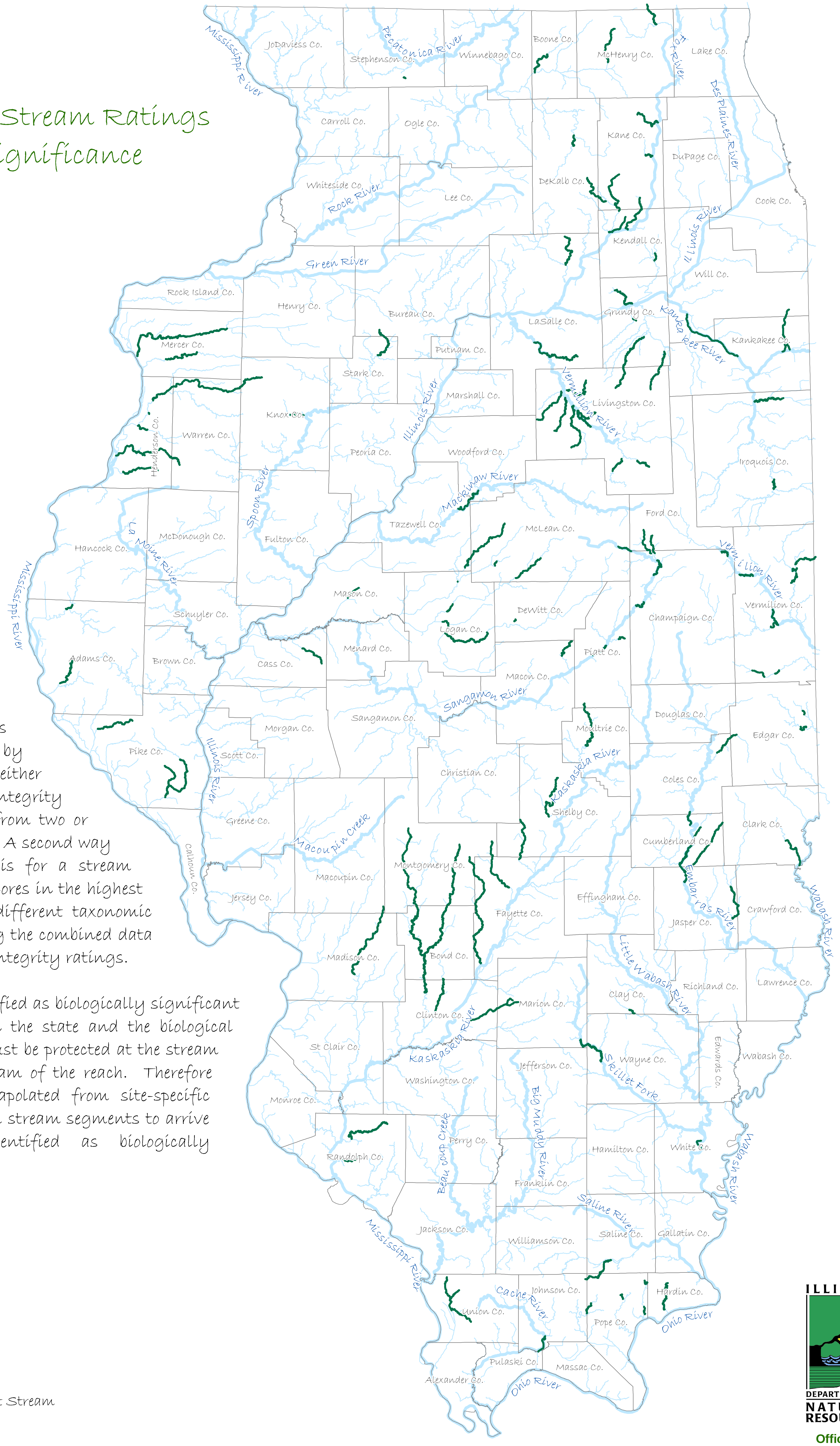
Exhibit I:

Biological Stream Ratings of Significance

Biological Stream Ratings for Significance



Biologically Significant Streams (BSS): streams that have a high rating or score based on data from at least two taxonomic groups. This can be achieved by obtaining an "A" rating either for diversity or for integrity that is based on data from two or more taxonomic groups. A second way to achieve this status is for a stream segment to have class scores in the highest class for at least two different taxonomic groups when considering the combined data from the diversity and integrity ratings.

Stream segments identified as biologically significant are unique resources in the state and the biological communities present must be protected at the stream reach, as well as upstream of the reach. Therefore BSS reaches were extrapolated from site-specific information to upstream stream segments to arrive at the segments identified as biologically significant.

〰 Biologically Significant Stream
〰 Major River
〰 Third Order or Larger Stream

ILLINOIS
DEPARTMENT OF
NATURAL
RESOURCES

Office of
Resource Conservation

September, 2008

Exhibit J:
Hunt Letter, August 2nd, 2007

Illinois Department of
Natural Resources
One Natural Resources Way • Springfield, Illinois 62702-1271
http://dnr.state.il.us

Rod R. Blagojevich, Governor
Sam Flood, Acting Director

August 2, 2007

Mr. Guy Hunt
Hillsboro Energy, LLC
925 S. Main Street
Hillsboro, IL 62049

Dear Mr. Hunt and Mr. Kimmle:

We received your draft information concerning the to-date drilling that has been completed at the potential future mine site in Montgomery County, Illinois. The Illinois Department of Natural Resources (IDNR) and the Illinois Environmental Protection Agency (IEPA) have reviewed the submitted data and offer the following informal comments:

1. Significant sand deposits were noted in borings 08-03-17-03 and 08-03-18-08, which may indicate the presence of Class I groundwater. Other borings indicate sand and gravel present at thicknesses around 5 feet. Hillsboro Energy, LLC should fully identify the materials and hydrogeologic conditions at the site, especially in both the proposed refuse disposal area (RDA) and the future RDA.

2. The lateral extent of the sand deposits found in borings 08-03-17-03 and 08-03-18-08 must be determined, as well as any other significant sand or sand and gravel deposits identified in the unconsolidated materials. This will require additional borings to be conducted throughout the site, but specifically in the vicinity of the proposed RDA's.

3. Both the IEPA and IDNR feel that the additional 4 borings proposed for the "eastern parcel of the permit area" are a good start, but additional drilling appears to be necessary throughout the site in order to adequately characterize the hydrologic properties of the unconsolidated materials, in light of the presence of the sand deposits noted in the borings above, as well as any additional borings conducted at the site.

4. All subsequent borings would need to be continuously sampled/logged paying close attention to the presence of sands/sand and gravels and saturated materials.

5. Hillsboro Energy would also need to conduct a survey of potable well use in the area to aid in the characterization study, and possibly aid in the development of geologic cross-sections and potentiometric maps.

6. The data submitted in the July 20, 2007 package, as well as all subsequent boring/drilling data collected, would have to be incorporated into the permit application, should you decide to apply for a permit for this site.

If you have any questions or comments on the above, please contact this office.

Sincerely,

Victoria M. Broomhead

Victoria M. Broomhead
Hydrologist

VMB:vb

cc: C. Johnson
V. Broomhead
A. Zimmer, IEPA

Exhibit K:

Memorandum re: Viable Technologies for Treating Coal Mine Stormwater Runoff

CARPENTER ENVIRONMENTAL ASSOCIATES, INC.

307 Museum Village Road
P.O.Box 656
Monroe, New York 10950
Phone: 845-781-4844
Fax: 845-782-5591
Senders E-mail: r.pape@cea-enviro.com

MEMORANDUM

Date: October 15, 2008

To: Sierra Club, Illinois Chapter

From: Robert J. Pape, P.E.

Re: Viable Technologies for Treating Coal Mine Stormwater Runoff CEA No. 08047

Carpenter Environmental Associates has been retained by Sierra Club, Illinois Chapter, to research viable technologies for treating stormwater runoff from coal mines. Mine stormwater runoff can contain a variety of metals as well as sulfate, chlorides, and total suspended solids (TSS). The following paper identifies technologies that have shown to be effective in removing these pollutants.

1) Bioremediation
Constructed wetlands and bioreactors are two types of bioremediation processes that are employed to treat mine runoff containing metals and sulfate.[1]

In general, constructed wetlands (CW) can be single or multi-basins designed to cultivate biology in an environment void of oxygen (anaerobic), or cultivate biology in an oxygen rich environment (aerobic). A multi-basin system can consist of both aerobic and anaerobic basins. Aerobic ponds and wetlands are effective for removing iron from net-alkaline mine water.[2] Anaerobic CWs commonly aim to establish a sulfate reducing bacteria (SRB) population. Production of SRB results in the precipitation of dissolved metals, including those found in mine run-off, as metal-sulfide complexes as well as reducing sulfate and increasing pH.[3]

Successive Alkalinity Producing Systems (SAPS) is a specific type of CW that consists of an organic mulch layer, limestone layer and a drainage system that has flushing capabilities to insure that iron and aluminum precipitates, which may be **contained in the mine runoff,** will not clog the cell.[4] SAPS can remove iron, aluminum, manganese, and sulfate as well as trace metals including barium, cadmium, chromium, copper, nickel, zinc and lead **as can be found in mine runoff**.[5] Runoff from a former coal mining operation in Gowen, Oklahoma, was treated using SAPS. Although actual data was not obtainable for the Gowen SAPS, the report regarding the Gowen SAPS found on the USEPA's website indicated that "concentrations of iron, aluminum, and manganese have decreased significantly" and the trace metals were reduced to near or below detection levels.[6,7] The success of this project spurred Oklahoma to use the Gowen SAPS design in at the Tar Creek superfund site in Ottawa, Oklahoma, and is being investigated for use in several watersheds nationwide and should be evaluated for coal mines in Illinois.[8]

A multi-basin wetland system was used in Albright, West Virginia, and in Springdale, West Virginia. These wetlands consisted of limestone rock drains and manganese-oxidizing bacteria to treat metal-contaminated leachate from a closed coal combustion byproduct landfill. The leachate entering these systems contain pollutants **similar to mine runoff**, specifically, iron, manganese and total suspended solids (TSS). The Albright CW treatment system reduced an influent stream containing: 2.5 mg/L total iron, 8.5 mg/L manganese, and 8 mg/L TSS to 0.3 mg/L, 1.1 mg/L, and 1 mg/L, respectively.[9] For comparison to the situation in Illinois, Albright's effluent are at or below the Deer Run Mine Draft NPDES Permit (Permit) levels for iron, manganese, and TSS. The Springdale CW treatment system reduced an influent stream containing: 12.5 mg/L total iron, 6.1 mg/L dissolved iron, 2.7 mg/L manganese, and 25 mg/L TSS to 0.3 mg/L, 0.1 mg/L, 0.2 mg/L, and 8mg/L, respectively.[10] Springdale's effluent concentrations are below the Permit levels for iron, manganese, and TSS.

Bioreactors are lined trenches, pits, or aboveground tanks that can contain a variety of materials as packing or have no packing and are entirely suspended growth reactors.[11] Bioreactors are either anaerobic or aerobic and can be a standard technology or proprietary technology. Like CWs, aerobic bioreactors can remove iron and aluminum.[12] Bioreactors that cultivate SRB biology can be used to eliminate metals commonly found in mine runoff, including iron and manganese, as seen with the SRB bioreactor system in Champagne Creek, Idaho which removed up to 91% of the iron in the influent waste stream.[13,14]

A pilot study on a standard technology type bioreactor investigated the effects of an aerated dolomite packed bed bioreactor and an aerated quartzite packed bed bioreactor on the reduction of manganese in mine water that is net-alkaline.[15] Each reactor was fed net-alkaline mine water containing 15 – 30 mg/L manganese. [16] The study concluded that these bioreactors reduced the manganese by 90 – 97%.[17]

One proprietary bioreactor system is ABMet®. ABMet® systems are configured for site specific waste streams and have been successfully used to treat mining water. [18,19] ABMet® has shown to remove selenium, arsenic, mercury, chromium, cadmium, copper, zinc, cobalt, nickel, antimony and nitrate. [20,21] Depending upon the ABMet configuration, these metals can be reduced 99+% and some metals can be reduced to 10 part per billion (ppb) or less.[22, 23]

Bioremediation has also been extensively used in the neutralization of acidic water (pH control), nutrient reduction and cyanide reduction.

2) <u>Reverse Osmosis</u>

Vibratory Shear Enhanced Process (VSEP) is a proprietary RO type process.[24] In addition to employing the technology of the pressure gradient across a membrane, VSEP adds "…torsional vibration of the membrane surface, which creates high shear energy at the surface of the membrane. The result is that colloidal fouling and polarization of the membrane due to concentration of rejected materials are greatly reduced." [25] A case study of VSEP treating acid mine water showed VSEP reduced the following constituents: total dissolved solids, calcium, magnesium, sodium, iron, manganese, copper, zinc and sulfates. Specifically, a mine water stream containing iron at 1,100 mg/L and sulfate at 8,000 mg/L were reduced to <0.1 mg/L, and 100 mg/L, respectively by VSEP.[26] A case study to treat an RO reject stream (the RO unit treated brackish well water) used VSEP as stage one of a two stage process and used a conventional spiral RO system as stage two. The RO reject stream contained similar pollutants such as chloride, sulfate and total dissolved solids **as does mine water runoff.** The study showed that VSEP reduced chloride, sulfate, nitrate, total dissolved solids, boron, and sodium. Specifically, an influent waste stream containing chloride at 3,285 mg/L, sulfate at 304 mg/L, and total dissolved solids at 7,314 mg/L were reduced to 628 mg/L, 25 mg/L, and 1,617 mg/L, respectively by VSEP.[27] The study also showed that the conventional spiral RO system produced a final treated water stream containing chloride at 11 mg/L, sulfate at 0 mg/L, and total dissolved solids at 51 mg/L. Both stages produce an effluent significantly below the Permit levels for sulfate and the two stage process reduces chlorides significantly below Permit levels.

3) Chemical treatment includes the addition of hydroxide or lime to the waste stream prior to the streams entry to a settling tank. Hydroxide and lime treatment removes metals using pH. Hydroxide and lime are added to a waste stream to achieve pHs that specifically correspond to the minimum solubilities of the metals being removed. Since different metals have their own minimum solubility at different pHs, several treatment stages may be necessary if multiple metals are to be removed from the waste stream.

   Chemical treatment also includes the addition of proprietary chemicals to reduce heavy metals or other constituents. Organosulfide TMT 15™ is a priority treatment chemical that can be added to the waste steam prior to a settling tank.[28] Organosulfide TMT 15™ promotes precipitation of cadmium, copper, lead, mercury, nickel, and silver from wastewater streams.[29] Organosulfide TMT 15™ is typically used as a second step reagent after the bulk of the metals are removed with hydroxide precipitation because Organosulfide TMT 15™ dosage is a function of stoichiometry. In an application in the coal burning Pleasant Prairie Power Plant, Organosulfide TMT 15™ is anticipated to reduce mercury in a flue gas desulfurization wastewater stream from <2,000 ug/L to 0.5 ug/L.[30]

4) Ion exchange removes unwanted ions from water by transferring them to a solid material (resins), in an ion exchanger, which accepts them while giving back an equivalent number of desirable ions contained in the ion exchanger. In the simplest terms, water softening is a form of ion exchange in which sodium, from salt, is exchanged with the calcium responsible for water "hardness." Selective Metal Ion Exchange has resins that have been tailored to removal of heavy metals including: copper, uranium, vanadium, mercury, lead, nickel, zinc, cobalt and cadmium.[31] Ion exchange has been used to treat mine wastewater for metals and nitrate removal. An example of this method being utilized for sulfate removal is at the Sierrita copper mine in Arizona.[32]

Attachments

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[1] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003.

[2] The Passive Treatment of Coal Mine Drainage, U.S. Department of Energy National Energy Technology Laboratory, Watzlaf, et. al., 2004

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[3] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003.

[4] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003.

[5] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003.

[6] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003.

[7] EPA Website Detailing Gowen, OK Alkalinity-Producing System Results, August 5, 2004. http://www.epa.gov/owow/nps/Section319III/OK.htm.

[8] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003.

[9] Applications of Passive Treatment to Trace Metals Recovery, Hoover, et.al.,

[10] Applications of Passive Treatment to Trace Metals Recovery, Hoover, et.al.,

[11] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003.

[12] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003

[13] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003

[14] Acid Mine Drainage: Innovative Treatment Technologies, Christine Costello, October 2003.

[15] Rapid Manganese Removal from Mine Waters Using an Aerated Packed-Bed Bioreactor, Johnson K. L., Younger, P. L., May 11, 2005

[16] Rapid Manganese Removal from Mine Waters Using an Aerated Packed-Bed Bioreactor, Johnson K. L., Younger, P. L., May 11, 2005

[17] Rapid Manganese Removal from Mine Waters Using an Aerated Packed-Bed Bioreactor, Johnson K. L., Younger, P. L., May 11, 2005

[18] Treatment Technology Summary for Critical Pollutants of Concern in Power Plant Wastewaters, Chu, P., January 2007.

[19] Water Online.com description of the Zenon ABMet process at http://www.gewater.com/products/equipment/ other_equipment/ABMet.jsp

[20] Treatment Technology Summary for Critical Pollutants of Concern in Power Plant Wastewaters, Chu, P., January 2007.

[21] Water Online.com description of the Zenon ABMet process at http://www.gewater.com/products/equipment/ other_equipment/ABMet.jsp

[22] Treatment Technology Summary for Critical Pollutants of Concern in Power Plant Wastewaters, Chu, P., January 2007.

[23] Water Online.com description of the Zenon ABMet process at http://www.gewater.com/products/equipment/ other_equipment/ABMet.jsp

[24] 2006 El Paso Desalination Conference, El Paso, Texas. A Comparison of Conventional Treatment Methods and VSEP, a Vibrating Membrane Filtration System, Johnson, Greg, Larry Stowell, and Michele Monroe, March 2006.

[25] 2006 El Paso Desalination Conference, El Paso, Texas. A Comparison of Conventional Treatment Methods and VSEP, a Vibrating Membrane Filtration System, Johnson, Greg, Larry Stowell, and Michele Monroe, March 2006.

[26] VSEP Filtration of Acid Mine Drainage: A cost-effective and efficient processing solution, Case Study, New Logic Research.

[27] 2006 El Paso Desalination Conference, El Paso, Texas. A Comparison of Conventional Treatment Methods and VSEP, a Vibrating Membrane Filtration System, Johnson, Greg, Larry Stowell, and Michele Monroe, March 2006.

[28] Treatment Technology Summary for Critical Pollutants of Concern in Power Plant Wastewaters, Chu, P., January 2007.

[29] Treatment Technology Summary for Critical Pollutants of Concern in Power Plant Wastewaters, Chu, P., January 2007.

[30] Treatment Technology Summary for Critical Pollutants of Concern in Power Plant Wastewaters, Chu, P., January 2007.

[31] Treatment Technology Summary for Critical Pollutants of Concern in Power Plant Wastewaters, Chu, P., January 2007.

[32] Sulphate removal demonstration plant using BioteQ's proprietary Sulf-IX ion-exchange technology (www.bioteq.ca)

Exhibit L:

Acid Mine Drainage: Innovative Treatment Technologies, October 2003

Acid Mine Drainage: Innovative Treatment Technologies

October 2003

Prepared by

Christine Costello

National Network of Environmental Management Studies Fellow

for

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Technology Innovation Office
Washington, DC
www.clu-in.org

NOTICE

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FOREWORD

About the National Network for Environmental Management Studies (NNEMS) Program

The U.S. Environmental Protection Agency (EPA) established the NNEMS program in 1986 to foster a growing interest among higher education students in environmental careers. The NNEMS program is a comprehensive fellowship program that provides undergraduate and graduate students an opportunity to participate in a fellowship project that is directly related to their field of study. The NNEMS program is sponsored by EPA's Office of Environmental Education.

Students who are awarded NNEMS fellowships are offered a unique opportunity to gain research and training experience directly linked to their undergraduate or graduate studies. NNEMS fellows conduct research projects to augment their academic studies, which EPA supports with financial assistance.

Each year, the NNEMS program offers approximately 50 to 60 research projects, developed and sponsored by EPA Headquarters in Washington, D.C. and EPA's ten regional offices throughout the U.S. The projects allow students to conduct research while working full-time at EPA during the summer or part-time during the school year.

CONTENTS

FIGURES

Purpose

Currently there is no comprehensive survey about the types of remediation technologies being used to treat abandoned mines. The purpose of this paper is to provide information about this topic with a particular focus on hard rock mining sites. Hard rock mines can be loosely defined as non-coal, metal mines, in the United States these mines are located in the Mid-West and Western states. This paper provides an overview of treatment technologies being used to remedy environmental problems at abandoned mine sites, with a focus on innovative treatment techniques.

1.0 Introduction

This report aims to identify abandoned mine sites that utilize innovative technologies to treat mine drainage or contaminated soils and to put that information into a database. Therefore, this paper is not a highly detailed description of a single technology, but rather an introduction to a variety of technologies currently used to treat mine sites in the country. A database was created to compliment this paper. It contains all of the case studies highlighted in this paper and quite a few other. It is available through the Technology Innovation Program website www.cluin.org. The goal of this database is to allow parties interested in implementing innovative treatments at AMD sites to learn from past successes and failures to advance these technologies.

A variety of sources were consulted to identify sites. Government agencies were the main targets as they are the most likely group to be addressing abandoned mines that presumably do not have a linked responsible party. Also, unlike consulting firms and private industry, i.e. the companies themselves, the government will generally disclose most technical information. The internet was used to look up information about the following agencies:

- Environmental Protection Agency - specifically the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, a.k.a. Superfund) and the Clean Water Act (CWA) programs;
- Department of the Interior - specifically the Office of Surface Mining, Bureau of Land Management (BLM), and United States Geological Survey (USGS);
- State environmental departments;
- Local environmental committees and community groups.

Another research avenue was grant distributions from CWA programs to local organizations. For example, Pennsylvania’s Growing Greener grant program funds many Abandoned Mine Land (AML) reclamation efforts in the name of improving local watersheds. This did not prove beneficial for every state. Where possible individuals were contacted through email and telephone for more specific information about programs and sites. As with any project an extensive literature review was done. Science Direct was searched, the Library of Congress catalog and on-line databases were also utilized and numerous conference proceedings were perused.

Due to the universe of abandoned mines, constantly evolving programs and projects this report does not imply a complete picture of all projects and programs in the nation. The report is, however, a start toward understanding what technologies are being used and some of the barriers to remediation, especially for non-traditional treatments. Appendix A includes brief summaries on the efforts being taken at the state level to address AML sites for selected states.

1.1 Background

Mining practices, present and past, cause environmental problems that can damage ecosystems and human health. Mining disturbs geologic formations that took millions of years to form; likewise, related natural systems and processes are disturbed, e.g. hydrology. Once disruption has taken place a variety of problems may arise, from physical hazards to pollution of water and soil. The most severe and widespread environmental problems almost always have to do with water, indeed all of the treatment technologies that will be discussed in this paper are designed for water or the prevention of water contact with solids.

There has been a lot of effort to quantify the universe of abandoned mines, the results vary. Some of the problem lies in definition. While some agencies define a site as a particular opening; others define a site as all of the openings at a particular location as one mine site. The Bureau of Land Management claims that estimates from Federal land management agencies, state and privately owned lands have ranged from about 80,000 to hundreds of thousands of small to medium-sized sites (U.S. Dept. of the Interior, 2003b). The Office of Surface Mining describes the problem in terms of money, “of the $8.2 billion of high priority [physical hazards] coal related AML problems in the AML inventory, $6.6 billion, 80%, have yet to be reclaimed; furthermore, “almost ninety percent of the $2.0 billion of coal related environmental problems in the AML inventory are not reclaimed. And this represents only a small part of the total problem as no systematic effort has been made to inventory these problems” (U.S. Dept. of the Interior, 2002a). To give one last perspective, the Mineral Policy Center, a non-profit organization, claims that there are 557,000 abandoned mines - mostly in the western United States (2003). Although it is difficult to say exactly how many sites exist, the number of abandoned mine sites in the US is enormous.

For roughly 25 years there have been efforts to address the dangers created by the past 250 - 300 years of large-scale mining in this country. The Surface Mining Coal and Reclamation Act (SMCRA), passed in 1977, requires a tax on coal production to be set aside in a fund for remediation efforts at abandoned coal mines. However, many abandoned mines are hard rock mines and are typically not eligible for SMCRA funding, though there are some exceptions. Other sources of funding may come from CWA grants, CERCLA grants or State funding. While there has been significant progress, there are still many sites without adequate funding. For example, California has no abandoned coal mines, therefore ineligible for SMCRA funding. A multi-stakeholder task force in California identified lack of funding as a key impediment to cleanup of abandoned mines in the state (see Appendix A). Some states have started to lobby for funding, for example, Colorado House Representative Mark Udall is seeking legislation that would create a fund for hard rock sites similar to that created by SMCRA.

Many states and agencies have only recently finished inventorying the number of sites and begun to evaluate sites to determine priorities for cleanup. States and other agencies that are doing remediation under SMCRA must address Priority 1 & 2 problems - those dealing with physical dangers - before they are able to use funding to address Priority 3 problems - environmental problems and/or high priority non-coal sites. The priority number system was defined by the U.S. Department of the Interior.

Due to limited resources, especially in the case of hard rock mines, innovative technologies can offer a plausible solution to the environmental threats created by abandoned mines. Traditional water treatments are modeled after wastewater treatment plants, which are machine intensive, chemical dependant, and require continuous operations and maintenance (O & M) staff. Traditional solid mine waste remediation tactics involve covering of piles and water diversion tactics which do not treat wastes but rather mitigate their impacts. The innovative technologies that will be discussed in this paper are largely passive treatment systems. Passive treatment systems are described as having little O & M costs, require little chemical application, and few if any mechanical devices (Hedin et al., 1994). Passive treatment systems can be a good solution for small drainage sites that might otherwise have few treatment options.

1.2 Chemistry

1.2.1 Acid Generation and Metals Leaching

Acid generation and metals dissolution are the primary problems associated with pollution from mining activities. The chemistry of these processes appears fairly straightforward, but becomes complicated quickly as geochemistry and physical characteristics can vary greatly from site to site. This paper will not describe these variables and their affects on chemistry, it will give an overview of the most common scenario found at coal and hard-rock sites with environmental concerns.

Pyrite (FeS_2) is responsible for starting acid generation and metals dissolution in coal and hard rock sites alike. When pyrite is exposed to oxygen and water it will be oxidized, resulting in hydrogen ion release - acidity, sulfate ions, and soluble metal cations, equation 1. This oxidation process occurs in undisturbed rock but at a slow rate and the water is able to buffer the acid generated. Mining increases the exposed surface area of these sulfur-bearing rocks allowing for excess acid generation beyond the water’s natural buffering capabilities.

$$2FeS_2\ (s) + 7O_2\ (aq) + 2H_2O \rightarrow 2Fe^{+2} + 4SO_4^{-2} + 4H^+ \qquad (1)$$

Further oxidation of Fe^{+2} (ferrous iron) to Fe^{+3} (ferric iron) occurs when sufficient oxygen is dissolved in the water or when the water is exposed to sufficient atmospheric oxygen.

$$2Fe^{+2} + \tfrac{1}{2}\ O_2 + 2H^+ \rightarrow 2Fe^{+3} + H_2O \qquad (2)$$

Some acidity is consumed in this process, however, the stage is set for further hydrogen ion release that will surpass these benefits. Ferric iron can either precipitate as ochre ($Fe(OH)_3$ the red-orange precipitate seen in waters affected by acid mine drainage) or it can react directly with pyrite to produce more ferrous iron and acidity.

$$2Fe^{+3} + 6H_2O \leftrightarrow 2Fe(OH)_3\ (s) + 6H^+ \qquad (3)$$

$14Fe^{+3} + FeS_2\ (s) + 8H_2O \rightarrow 2SO_4^{-2} + 15Fe^{+2} + 16H^+$ (4)

When ferrous iron is produced as a result of equation 4 and sufficient dissolved oxygen is present the cycle of equations 2 & 3 is perpetuated (Younger, et al, 2002). Without dissolved oxygen equation 4 will continue to completion and water will show elevated levels of ferrous iron (Younger, et al, 2002).

Once the waters are sufficiently acidic, acidophilic bacteria - bacteria that thrive in low pH - are able to establish themselves. Microorganisms can play a significant role in accelerating the chemical reactions taking place in mine drainage situations. *Thiobacillus Ferroxidans*, a bacteria, is commonly referenced in this case. These bacteria catalyze the oxidation of ferrous iron, further perpetuating equations 2 through 4. Another microbe belonging to the Archaea kingdom, named *Ferroplasma Acidarmanus*, has recently been discovered to also play a significant role in the production of acidity in mine waters (Lauzon, 2000).

Though not a major source of acidity, the generation of hydrogen ions when certain metals form precipitates, must be taken into account when considering treatment options.

$Al^{+3} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$ (5)
$Fe^{+3} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+$ (see equation 3) (6)
$Fe^{+2} + 0.25\ O_2(aq) + 2.5\ H_2O \leftrightarrow Fe(OH)_3 + 2H^+$ (7)
$Mn^{+2} + 0.25\ O_2(aq) + 2.5\ H_2O \leftrightarrow Mn(OH)_3 + 2H^+$ (8)

Other metals commonly found in mine drainage waters exist because they are present in the rocks, similar to pyrite. For example, there are a variety of other metal sulfides that may release metal ions into solution, but may not generate acidity (Younger et al., 2002) the reasons for this are not clear. Including:

Sphalerite	$ZnS(s) + 2O_2(aq) \rightarrow Zn^{+2} + SO_4^{-2}$	(9)
Galena	$PbS(s) + 2O_2(aq) \rightarrow Pb^{+2} + SO_4^{-2}$	(10)
Millerite	$NiS(s) + 2O_2(aq) \rightarrow Ni^{+2} + SO_4^{-2}$	(11)
Greenockite	$CdS(s) + 2O_2(aq) \rightarrow Cd^{+2} + SO_4^{-2}$	(12)
Covellite	$CuS(s) + 2O_2(aq) \rightarrow Cu^{+2} + SO_4^{-2}$	(13)
Chalcopyrite	$CuFeS_2(s) + 4O_2(aq) \rightarrow Cu^{+2} + Fe^{+2} + SO_4^{-2}$	(14)

Metals are naturally dissolved from weathering slowly over time. The dissolution process is sped up when the pH of the water strays from near-neutral, that is at either high or low pH - in the case of mine drainage low pH is the more plausible scenario (Younger et al., 2002; Blowes et al., 2000). For more information see Chapter 2 of Mine Water: Hydrology, Pollution, Remediation by Younger et al., 2002.

1.2.2 Neutralization and Metals Removal

The ways by which metals precipitate have seemingly endless possibilities and are not always well understood. By far the most common application for reducing acidity and adding alkalinity is lime. There are many ways to treat mine drainage through enhanced natural processes which form the basis for passive treatments. There are many aerobic and anaerobic process that lead to metals precipitation that are commonly practiced. Though not complete the following information should provide some insight about the technologies that will be discussed shortly.

It is very important to gain control of the pH of the drainage because pH effects many things including the solubility of metals and the kinetics of the oxidation and hydrolysis processes (EPA, Vol.4). In addition, the relationship between pH and metal removal processes varies among metals and also between biotic and abiotic processes (EPA, Vol. 4)

Limestone (calcium carbonate), rich in calcite, increases the pH of water by consuming hydrogen ions and adding alkalinity through bicarbonate ions (Younger et al., 2002).

$$CaCO_3 + 2H^+ = Ca^{+2} + H_2O + CO_2 \qquad (15)$$
$$CaCO_3 + H_2CO_3 = Ca^{+2} + 2HCO_3^- \qquad (16)$$

Once the pH of the acidic water has been raised metals can precipitate more easily to form hydroxides and oxyhydroxides, in some cases the pH alone will change the metal ion to an insoluble form, this is true in the case of aluminum.

Other commonly used alkaline agents are hydrated lime (calcium hydroxide), soda ash (sodium carbonate), caustic soda (sodium hydroxide), and in some cases ammonia (U.S. Dept. of the Interior, 2002b).

The processes involving metals more common to coal mining regions (iron, aluminum, and manganese) are fairly well understood. The removal of iron is better understood than other metals common to drainage sites, which may be one of the reasons why passive treatments are more common in the East. Iron can form oxyhyroxides (FeOOH) or hydroxides ($Fe(OH)_3$) under aerobic conditions or a sulfide solid under anaerobic conditions. Iron and manganese (Mn) precipitation processes are related in that the precipitations are sequential in aerobic conditions (EPA, Vol. 4). Iron oxidizes and precipitates more quickly than Mn because oxidized Mn solids are unstable in the presence of Fe^{+2} therefore the levels must be reduced significantly before Mn can be converted to stable solid precipitates (EPA, Vol. 4). Manganese under aerobic conditions can form an oxyhydroxide (MnOOH) and oxides (Mn_3O_4 and MnO_2) and in alkaline environments a carbonate ($MnCO_3$) (EPA, Vol. 4). Manganese sulfide is highly soluble and therefore highly unlikely to remain precipitated if it should form under anaerobic conditions (EPA, Vol. 4).

Aluminum is removed from waters by maintaining the pH between 5 and 8, where $Al(OH)_3$ is highly insoluble; the passage of mine water through highly oxidized or reduced environments has no effect on Al concentrations (EPA, Vol. 4).

Technologies designed to remove metals common to hard rock mining almost always involve the establishment of sulfate reducing bacteria (SRB), which can be difficult in cold climates. Sulfate reducing bacteria remove metals from solution as precipitates as a result of their survival (Zaluski et al., 2000). SRB reduce sulfate to soluble sulfide when provided with an organic carbon source, i.e. compost; as a result of this process acetate and bicarbonate ion are also produced. The soluble sulfide reacts with the dissolved metals to form insoluble metal sulfides, equation 18; the bicarbonate ions increase the pH and alkalinity of the water, equation 17 (Zaluski et al., 2000). Bicarbonate also allows for the possible production of Zn, Cu, or Mn carbonates (Macalady, 1998). Metals likely to form insoluble sulfide precipitates include: Cu, Zn, Cd, Pb, Ag, and Fe(II) (Macalady, 1998). These processes are summarized by the following reactions:

$$SO_4^{2-} + 2CH_2O \longrightarrow H_2S + 2HCO_3^- \qquad (17)$$
$$H_2S + M^{+2} \longrightarrow MS + 2H^+ \qquad (18)$$

In addition to precipitation processes, metals can be removed from water through a variety of methods common to wetlands, and seen in technologies utilizing organic matter and/or vegetation:

- filtering suspended and colloidal material from the water
- uptake of contaminants into the roots and leaves of live plants
- adsorption or exchange of contaminants onto inorganic soil constituents, organic solids, dead plant material or algal material
- neutralization and precipitation of contaminants through the generation of HCO_3^- and NH_3 by bacterial decay of organic matter.
- destruction or precipitation of chemicals in the anaerobic zone catalyzed by the activity of bacteria
- destruction or precipitation of contaminants in the aerobic zone catalyzed by the activity of bacteria (EPA, 1993b).

It is not in the scope of this paper to describe all of the potential considerations related to each metal of concern; a few examples have been mentioned to illustrate the necessity of carefully analyzing all of the metal contaminants and the surrounding hydrologic, geologic, chemical, and biologic situation in order to properly design for removal.

1.3 Environmental Concerns

Environmental damage or pollution associated with mines nearly always has to do with a decrease in pH and/or elevated concentrations of heavy metals in nearby waters and soils. There are instances were one problem occurs without the other, for example circum-neutral pH and elevated metals concentrations or vice versa. Debris from waste piles may be blown and contaminate surrounding areas with metals. Silt and sediments may run-off into nearby streams and obstruct water flow. Other sources of pollution that may not initially come to mind are abandoned buildings and industrial equipment that contribute to pollution, including waste drums, heavy equipment, batteries, etcetera.

While all of these problems are serious, the main focus will be on polluted water resulting from mine drainage. Indeed, with the exception of a few new means of revegetation, most of the innovative technologies in the literature address water treatment.

Younger et al., provide information about the impacts that mining has on the water environment, they have defined six distinct impacts (2002). Not all of these impacts deal with pollution, but it is useful to consider all of the potential problems for a holistic view useful for designing an effective remediation plan.

Figure 1. Air compressor at an abandoned mine site in Leadville, CO.

1) "*The mining process itself*"(pp. 55) Which is associated with the disruption of groundwater hydrology. It has been pointed out that, "the miner and the water resource manager share a common interest in avoiding the ingress of fresh water into a mine void; the water manager's loss of resource is the miner's increase in nuisance" (pp. 57).

2) "*Mineral processing operations*" (pp. 57). For example, cyanide leaching operations, gold-mercury amalgamation. Contaminated abandoned leach pads can contribute to polluted runoff from the mine site. Active mines today, at least in the U.S., have regulatory obligations to prevent this type of contamination.

3) *The dewatering which is undertaken to make mining possible*. Some of the problems that can arise from pumping water out of mining shafts include: water table depression resulting in reduction in water availability for residents and the surrounding hyrdologic system, i.e. wetlands, streams, lakes; land subsidence or collapse; and, surface or groundwater pollution if mine water is of poor quality and runs to nearby waterways. However, mining industry today takes some measures to reduce these impacts through: compensation flows, in which water is added to sensitive surface waters, and may even be treated and pumped to specific locations; local re-injection of groundwater; alternate water supplies might be provided for affected residents; and/or waters that are unaffected by the mining operation itself, but are not of good quality might be treated before discharge.

4) *Seepage of contaminated leachate from waste rock piles and tailings dams*. For example, waste rock piles may not have had enough metal present to be economical to recover; however, the rock material might have sufficient pyrite present to generate acidity and mobilize metals.

5) "*The flooding of abandoned mine workings after mining has ended" or, "water table rebound*" (pp.59). While the water table is recessed and pyrite is able to oxidize causing a build-up of "acid-generating salts," when the water table rises these salts are dissolved causing an increase in pH and dissolved metals (pp. 60). There are other possible hazards like erosion of support columns in the mine tunnels leading to subsidence and also, the converse rising ground levels due to rehydration of soils, especially clays.

6) *Discharge of untreated mine water after flooding of workings* can lead to: surface water pollution, pollution of overlying aquifers, localized flooding and overloading and clogging of sewers.

For more information about environmental concerns associated with abandoned mines see EPA, 2001, chapters 2 & 3 and Younger et al., 2002.

2.0 Treatment

Treatment of mine sites generally requires pH adjustment, oxidizing or reducing (redox) conditions, and/or stabilization of wastes. Treatment technologies will be broken up into this categories: traditional and innovative. It is difficult to assign absolute definitions, the following distinctions will help to clarify the meanings.

2.1 Traditional

Traditional treatments rely on conventional, well-recognized technology to raise pH or create redox conditions. The types of technologies considered traditional in this paper include: water treatment plants, relocation of wastes, covering of waste piles, water diversion tactics, and in some cases revegetation.

Traditional or conventional treatments for mine waters are those that follow the pattern of an ordinary wastewater treatment plant often referred to as active treatment. Younger et al. define "active" treatment as "...the improvement of water quality by methods which require ongoing inputs of artificial energy and/or (bio)chemical reagents" (2002, pp. 271). There are a variety of methods that are considered "active," the most predominate one is "ODAS" - oxidation, dosing with alkali, and sedimentation (Younger, et al., 2002). The process is similar to that of traditional wastewater treatment plants. Others traditional or "active" treatments common to wastewater treatment plants include: sulfidization, biosedimentation, sorption and ion exchange, and membrane processes like filtration and reverse osmosis (Younger, et al, 2002). The waters are removed from their course, treated and then discharged.

Depending on the situation it may be advantageous to install a traditional water treatment system as described above, in some cases it might even be the only option. One of the advantages is precision. For the most part an engineered system can be altered to obtain desired discharge regardless of the changes in the incoming water characteristics. This can be useful for active mining sites with frequently changing water characteristics (Younger, et al., 2002). For instance, Russ Forba who works on the Berkeley Pit Superfund site in Montana, stated that after evaluation of the options they did not feel comfortable with the reliability and contaminant removal efficiencies associated with innovative treatments due to the seven million gallon-per-day flow and complex characteristics of the wastewater (R. Forba, personal communication, 6/20/2003). Another benefit is that the land required to establish a plant for large flows is much smaller than the space required for comparable passive treatment systems (Younger et al., 2002). Finally, traditional wastewater treatment plants are accompanied by a large body of experience and information, making the expertise easier to find and with a higher confidence level in performance.

Traditional treatment approaches to handling solid mine wastes include a variety of excavation, landscape adjustment, and stabilization techniques. Again, in most cases the main concern is to avoid water infiltration of the solid wastes. Solid wastes can be contained on-site in a variety of ways: lined pits, un-lined pits, clay or plastic caps, etc. Similarly, wastes can be shipped off-site to landfills, treatment plants, or recovery operations; however, this option may be costly as prices are by the ton. Covering or "capping" wastes is a fairly common choice, the cover can be multiple layers of plastic, cement, soil, compost, rock, vegetation, etc. The idea behind these methods is that the solid materials high in metals and/or acid-producing materials will not be exposed to the elements and will not cause typical problems associated with mine wastes. While these solutions may be a reasonable option for reducing potential harm to humans and the environments they generally do not reduce the toxicity or volume of the metals present in the soils (Pioneer Technical Services, 2002).

Re-grading is a common term used in describing remediation efforts. Re-grading is simply reducing the slope of a waste rock or tailings pile to prevent erosion by reducing water runoff and to provide a more stable surface to enhance revegetation efforts. Another tactic to control water flow near a waste pile is to attempt to divert water from the pile by installing trenches and culverts.

Whether revegetation is traditional or innovative is somewhat obscure. It is not a new idea and has been done for many years. However, some new methods have made it possible to revegetate areas that were previously thought to be a lost cause. For example, biosolids and lime applications have been proven to be a viable method for establishing self-sufficient vegetative cover. The distinction between innovative and traditional lies between the goal and outcomes of establishing vegetation. If the goal or outcome is to reduce toxicity or to recover metals then it would probably be considered an innovative treatment; if the goal is to prevent metals contaminated soils from being blown into nearby yards, but the metals are still present in the same quantities it would probably be considered traditional.

For more information about available treatment technologies please see: EPA's Abandoned Mine Site Characterization and Cleanup Handbook, Chapter 10.

Case Study: California Gulch, Leadville, Colorado

The California Gulch Superfund site located in Leadville, Colorado utilizes nearly every traditional treatment option described above and even some innovative applications. Some of the treatments include: two water treatment plants, consolidation and stabilization of piles, water diversion, capping, revegetation, and biosolids application. Mining for gold, silver, copper, zinc, manganese, and lead began in 1859. The site is approximately 16.5 square miles, divided into twelve Operable Units (OUs) (EPA, 2003). Each OUs is managed by a different party including EPA, the U.S. Bureau of Reclamation, the State of Colorado, and ASARCO, the Resurrection Mining Company, a subsidiary of Newmont Gold Company, and the ASARCO-Resurrection joint venture (EPA, 2003).

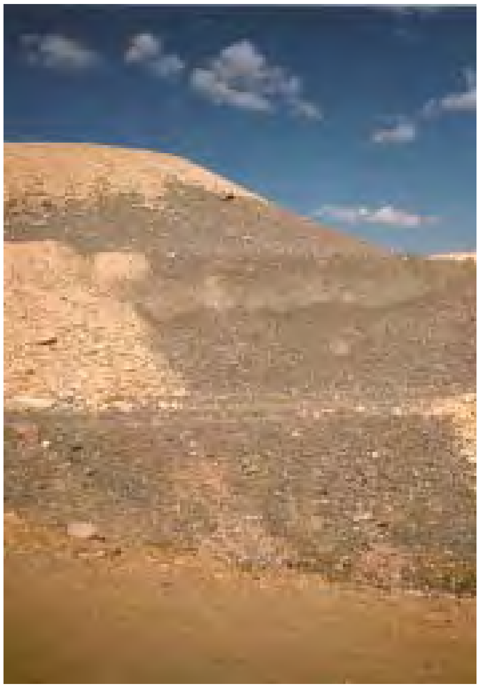

Figure 2. Capped waste pile in Leadville, CO. Photo taken by author.

The two water treatment plants are located at the outfall of abandoned mine tunnels: the Yak Tunnel and the Leadville Mine Drainage Tunnel. Tunnels were built to transport ores out of mines and sometimes drain groundwater to allow access to the underground. Rock in these tunnels is highly disturbed and exposed to water and oxygen therefore, pyrite oxidation and metals leaching is likely and effluent from the tunnels is highly problematic. The treatment plant at Yak Tunnel is managed by the ASARCO-Resurrection joint venture. The flow to the plant is highly dependent on season, during summer months there can be little more than a trickle of water but in the spring during snowmelt the flow increases dramatically. Before the plant was in operation nearly 210 tons of metals entered the Arkansas River annually (EPA, 2003). The second treatment plant is at the end of the ten mile long Leadville Mine Drainage Tunnel. This plant is managed by the Bureau of Reclamation. In addition to treating water that has made its way into the tunnel, it receives runoff from tailings piles located near the origin of the tunnel from tailings & waste rock piles. Furthermore, it is believed that nearly two-thirds of the water reaching the tunnel is runoff and groundwater that is uncontaminated before entering the tunnel (M. Holmes, personal communication, 7/22/2003). If this groundwater could be diverted from the tunnel the treatment plant would be more efficient in treating the drainage. However, this is easier said than done given the depth of the tunnel and the complexity of the hydrology at the site. The current thought is to install a plug to block flow of clean water into the tunnel; but, in order to do this a shaft would have to intersect the tunnel at a depth of 500 feet below ground level (M. Holmes, personal communication, 7/22/2003). Aside from being expensive it is difficult to drill accurately enough to intersect the tunnel at an appropriate location (M. Holmes, personal communication, 7/22/2003). Further complications would arise with the construction and performance of the plug.

Given the highly variable flow patterns and difficult climate at the elevation of 10,162 feet water treatment plants are a good option for treatment at the California Gulch site. In addition, when passive treatment was considered using wetlands it was determined that the space needed for construction would consume the entire town of Leadville (M. Holmes, personal communication, 7/22/2003).

Consolidation of waste piles is another large effort taken at the site to reduce water quality impacts. More than 350,000 yards of contaminated soils, sediments, and mine processing wastes have been consolidated on site (EPA, 2003). Once consolidated, a variety of measures have been taken including diversion trenches and culverts, evaporation ponds, and capping to minimize contaminated runoff leaving the site. Diversion trenches attempt to catch runoff before it comes into contact with the waste pile thereby avoiding contamination of the water so that it might reach the river or other water body in a “clean” state. Evaporation ponds collect runoff from piles and allow water to evaporate leaving metal precipitates, mostly iron, to stay in the pond. A couple of piles have been capped to prevent water infiltration and runoff. Revegetation efforts are also underway at many locations on the site, some of the locations have used the application of biosolids which will be describe in the Innovative Technologies section of this paper. All of these efforts have helped to reduce water quality issues in the Arkansas River.

2.2 Innovative

What is considered innovative? The Encarta English Word Dictionary provides some insight, the technology should be attempting to change the properties or form of a chemical, here the hydrogen ion and metal ions, in a way that has not been attempted in recent years:

> *innovative* is defined as: "new and original: new and original or taking a new and original approach"
>
> *treatment* is defined as: "technology: treating something with agent: an act of subjecting something to a physical, chemical or biological process or agent" (2003).

Though "innovative treatment" could surely describe a wide range of technologies, for example chemical encapsulation of wastes, the discussion here is limited to full-scale implementation of new technologies that have been installed at multiple abandoned mine sites. A variety of "passive treatments" have become the most predominate innovative treatments applied aside from traditional choices. Passive treatments are considered to be those that treat waters or solids using enhanced natural processes, in-situ and require minimal upkeep (Hedin et al., 1994; Younger et al., 2002). Research into these techniques began as early as thirty years ago and has been growing ever since.

The beginning of this movement developed out of the observation that wetlands naturally remove metals from contaminated water (Gusek, 1998). Through trial and error it was discovered that in many instances plants were not necessary to treat the waters, rather other biochemical and geochemical reactions were responsible for water quality improvements (Gusek, 1998). For metals common to hard rock mining (Zn, Pb, Cd, As, Mo, Au, Ag, to name a few) sulfate reduction by bacteria is usually the premise behind the design of passive treatment with the goal of inducing metal precipitation as sulfides. For metals common to coal mining (Fe, Al, and Mn) aerobic processes, with or without an alkaline agent are the most commonly applied applications. Another major player in passive treatment are alkaline agents, most commonly lime, although the application of lime to reduce acidity it not particularly innovative, some of the ways to expose the acidic waters to the alkaline agent are innovative.

Many of the innovative technologies in operation are based on the same principles. Permeable Reactive Barriers (PRBs), bio-reactors, and constructed wetland technologies can all utilize alkaline agents and sulfate reducing bacteria to treat mine drainage. The majority are in-situ applications that manipulate natural processes to treat acidic and/or metals contaminated water, the exception is the use of iron in PRBs to treat uranium, see pages 25-26. Their differences lie in construction and water source. PRBs have a subsurface reactive section that groundwater flows through following its natural course to be treated, in some cases there are impermeable walls to direct the flow of the water to the reactive section. The reactive media is usually compost material that hosts sulfate reducing bacteria, though there are a few others. Bioreactors are somewhere between a PRB and a wetland, water - ground or surface - flows through and natural reactions work to remove metals. Whether subsurface or exposed to the atmosphere, bioreactors are generally lined, filled with composted materials and/or alkaline agents, and in some cases include vegetation. Constructed wetlands are very similar to both PRBs and bioreactors, they are often lined ponds filled with organic matter and/or alkaline agents and sometimes vegetation. Organic matter and vegetation allow an opportunity for metals to absorb and/or adsorb to organic surfaces, this is true for bioreactors and PRBs as well. Anaerobic wetlands aim to promote the growth of sulfate-reducing bacteria and raise pH. Aerobic wetlands are most often used for net alkaline waters, oxygen infiltration is encouraged and metals precipitate as oxyhydroxides, hydroxides, and carbonates. Both bioreactors and wetlands almost always include collection and piping systems, while PRBs are simply placed in the flow path.

Lime-based applications considered innovative in this paper, are anoxic limestone drains and Successive Alkalinity Producing Systems (SAPS). The latter is very similar in construction and theory to wetlands/bioreactors and is also an improvement to the anoxic limestone drain technology.

2.2.1 Limestone Drains

Anoxic Limestone Drains (ALDs) treat acidic and potentially metals-laden waters by sending them through an underground pathway that is packed with crushed limestone. ALDs typically outlet into a settling pond or wetland to allow metals an opportunity to precipitate and settle (Cravotta, 2002).

The problem with ALDs is that they often experience armoring - described as strong adhesion and complete pacification by encrustation - causing the limestone to become inactivated and potentially cause clogging of the drain (Cravotta, 2002; Sasowsky, 2000). To effectively install an ALD many suggest that dissolved oxygen, Fe^{+3}, and Al^{+3} concentrations be less than 1 mg/L; some authors have suggested that Fe^{+3} and Al^{+3} concentrations can be higher, between 1 and 5 mg/L (Cravotta, 2002). In either case this is a very low threshold when dealing with mine drainage.

A study by Sasowsky et al., suggests that the armoring of limestone can be substantially offset by incorporating sandstone into the drain (2000). Sasowsky et al., observed that when acidic and metals contaminated drainage at Big Laurel Creek at the East Fork Obey River in Tennessee discharged onto both exposed limestone and sandstone the majority of metallic oxides precipitated onto sandstone rocks (2000). This suggested a preferred precipitation media. In order to validate that the observed precipitation was not merely coincidence or mechanical, laboratory and field test at another mine drainage location in Silver Creek, Ohio were conducted. Similar results were recorded, and sandstone had an order of magnitude higher iron precipitation than limestone (Sasowsky et al., 2000). If this preference is fairly consistent, the addition of crushed sandstone to limestone drains could reduce armoring of limestone. It might also be noted that these studies were not conducted at oxygen deficit locations, and so behavior in anoxic conditions should be investigated.

Figure 3. Burleigh Tunnel, 7/2003, photo taken by the author

Case Study: North Pennine Orefield, UK

An emerging potential use for ALDs is for zinc removal. Nuttall & Younger (2000) conducted a field-scale test to use an ALD to remove zinc from net alkaline waters. The pilot scale ALD was place in the Nent Valley within the North Pennine Orefield, United Kingdom, the area had been mined for over two centuries for lead and zinc (Nuttall & Younger, 2000).

Metals leach from spoil heaps and tailing dams; contaminated land drainage and five abandoned mine adits also discharge metals into the River Nent. The waters have high hardness values, high alkalinity, and pH in the range of 7.4 to 8.0. The dissolution of sphalerite, ZnS (see equation 5), results in zinc concentrations in the range of 3 to 8 mg/L; there are also concentrations of lead, cadmium (both well below 1 mg/L), and arsenic (Nuttall & Younger, 2000). Geochemical modeling and laboratory tests revealed that raising the pH from approximately 7.5 to 8.2 would result in the optimal reduction of zinc in solution (Nuttall & Younger, 2000).

Aerobic processes that aim to result in hydroxide or sulfite solids have not been successful in this case because in hard, net-alkaline waters zinc is predominantly present as carbonate complex ($ZnCO_3^0$) and will not readily form non-carbonate solids (Nuttall & Younger, 2000). Therefore, an anoxic limestone drain was chosen as a possible way to raise the pH to roughly 8.2 for optimal removal (Nuttal & Younger, 2000). The results of the pilot test show 22-percent reduction in zinc concentrations after passing through the anoxic limestone conditions, with a retention time of 14 hours (Nuttall & Younger, 2000).

This is not the typical example, most ALD installations have been at coal drainage sites. It is particularly interesting because it does not rely on microorganisms which tend to be more temperature dependent, so the application might be possible at colder temperature sites.

2.2.2 Constructed Wetlands

There are two types of wetlands used to treat mine drainage, aerobic and anaerobic/compost. As mentioned previously, observations by ecologists that wetlands are capable of treating water and/or retaining toxics forms the basis of most passive treatment technologies.

It is possible for mine drainage to be net alkaline. If the metal of concern is iron an aerobic wetland is the best treatment option; aerobic treatment alone is rarely successful with other types of metals. Net alkaline waters are able to buffer the additional hydrogen ions released during metal hydrolysis reactions, for example: $Fe^{+3} + 2H_2O \text{ --> } FeOOH + 3H^+$ (EPA, Vol. 4). The precipitation of metals is a purely chemical reaction and is not as temperature dependent as sulfate precipitation common to anaerobic wetlands (EPA, Vol. 4). The main limiting factor for these systems is metal precipitate build-up, these deposits may need to be removed to allow for continued wetland operation. Robert Hedin has started a company that dredges this build-up and sells it for use as pigment in dyes and paints.

When waters are net acidic, the pH must be raised and ideally the waters will be bought to net alkaline conditions. When iron and aluminum are the main contaminants then alkaline addition followed by an aerobic settling pond is often used to precipitate metals and raise pH. The most common wetland application for hard rock mines aims to establish sulfate-reducing bacteria under anaerobic conditions and, as a result of the bacteria's metabolic needs, metals are precipitated as sulfides, see equations 17 &18. Anaerobic wetlands generally consist of organic substrate, often compost, and can be mixed with lime to increase alkalinity (EPA, Vol. 4).

There are a variety of considerations when designing a constructed wetland, more information can be obtained in EPA's Volume 4: Coal Mine Drainage; Younger et al., 2002; and, Macalady, 1998.

Case Study: Burleigh Tunnel, part of the Clear Creek/Central City Superfund Site, Colorado

This site is located in Idaho Springs, Colorado in a narrow valley with very harsh cold winters and limited sunlight year-round. This project was in operation for about 3 years before treatment failed for a variety of reasons and was decommissioned.

The water exiting the Tunnel is roughly neutral with a pH of 6.5, with discharge averaging 60 gallons per minute, elevated concentrations of bicarbonate buffer the mine water, and zinc is the metal of most concern (J. Lewis, personal communication, 7/7/2003). The pilot system installed is described as two "anaerobic compost wetlands in both upflow and downflow configurations," they were not designed to treat the entire flow, but only one-fourth, or 15 gpm - approximately 7.5 gpm in each cell (EPA, 2002b).

Each wetland was a 0.05-acre (2178 ft^2) cell (a.k.a. "pit") filled four feet deep with a mixture of an organic-rich compost (96 percent) and alfalfa hay (4 percent). The cells were installed below grade to reduce freezing and the earthen side walls were bermed.

The base of each cell was made up of a gravel subgrade, a 16 ounce geofabric, a sand layer, a clay liner, and a high-density polyethylene liner (EPA, 2002b). Geonets and geofabrics were applied in order to: separate influent and effluent piping; hold compost in place in the upflow cell; separate perforated PVC piping from the compost (EPA, 2002b). The geonet and perforated piping ensured even distribution of the influent water into treatment cells and prevented short-circuiting of water through the cells. For more details consult the EPA "SITE Technology" publication listed in the bibliography as EPA 2002b.

The hydraulic system for the cell involved concrete v-notch weirs, one for influent and effluent for each cell. At some point the valves in the downflow cell became locked-up and could no longer be operated; the time and reason are unknown (J. Lewis, personal communication, 7/16/2003). Water entered the upflow cell under pressure at the bottom of the compost and exited from the top; water entered the downflow cell at the top and flowed down by gravity, exiting at the bottom (EPA, 2002b). A drainage collection structure was built within the Tunnel to build sufficient hydraulic head to drive flow through the two cells (EPA, 2002b). A bypass system was also constructed, though was not always effective (J. Lewis, personal communication, 7/16/2003).

During its three years in operation the upflow wetland removed an average of 93 percent of zinc the first year and 49 and 43 percent during the second and third years (EPA, 2002b). The downflow wetland removed a mean of 77 percent of the zinc during the first year and 70 percent the second year; flow was discontinued in the third year (EPA, 2002b). Based on aqueous geochemical modeling, observations of cell compost, results of the sulfate-reducing bacteria count, and acid volatile sulfide data, biological sulfate reduction was not the main removal mechanism. Primary removal is thought to have occurred due to precipitation of zinc oxides, hydroxides, and carbonates in aerobic portions of the cell. The upflow cell during the first six months of operation had effluent levels of less than 1mg/L; concentrations began to increase near the end of 1994 into 1995, by May 1997 concentrations had reached 60.1 mg/L (EPA, 2002b). The cell suffered a significant blow in the spring of 1995. Heavy runoff increased the flow through the cell to 20 gpm of aerobic water, and the increased flow also apparently mobilized more zinc and substantially increased the zinc concentrations. After the increased flow, removal efficiencies were around 43 to 49 percent, whereas before removal efficiency were more than 90 percent. In 1997 a visibly obvious preferential flow path developed and was eliminated. The upflow cell was decommissioned in June of 1999. It is believed that the initial high removal rates in the upflow cell are the result of adsorption and absorption along with biological sulfate reduction; decline in removal rates is speculated be related to the decline in SRBs.

Currently there is no treatment being done at the Tunnel. The water seems to be entering the subsurface, it is unclear whether it is building up on the site, draining from the site, or traveling as groundwater; however, sampling of water is indicating that zinc concentrations are within regulatory standards of less than 200 micrograms/liter, the reason is undefined (J. Lewis, personal communication, 7/16/2003).

This example is interesting because the design was to precipitate metal sulfides under anaerobic conditions, yet the predominate form of precipitate was that common to aerobic conditions. It would be useful to gather information on the potential precipitates under aerobic conditions, especially abiotic reactions.

2.2.3 Bioreactors

Passive bioreactors are lined trenches or pits that can contain a variety of materials, most commonly a mixture of cobbles, compost, other organic matter, and/or an alkaline agent. Sometimes above ground tanks containing any variety of materials including those described above and other trickling filter types of materials - common in bio-treatment of municipal wastewater treatment used to establish appropriate microorganisms to precipitate metals and adjust pH - are referred to as “bioreactors.” The tank type of bioreactor will not be discussed in this paper, though they are used to treat acid mine drainage. They are both legitimate in using the term, “bioreactor” as they are using biological reactions to treat the waters. Arguably, the term "bioreactor" would in fact include PRBs, SAPS, and wetlands. The distinction between them has been made because the literature does so.

A. Case Study: Silver Bow County, Montana

Sulfate Reducing Bacteria (SRB) are the key to these bioreactors installed at the Calliope abandoned mine site in Silver Bow County, Montana in the Fall of 1998 (Zaluski et al., 2000). This project was funded by the EPA and jointly administered by the EPA and the Department of Energy; the project was implemented by MSE Technology Applications in Butte, MT. Water that flows through a collapsed adit discharges onto a large waste rock pile, upon exiting the pile the water has an average pH of 2.6 and elevated metals concentrations; this water then flows into a pond resulting in a pH of 3 to 5.5 depending on mixing ratios largely determined by the season. In order to treat the mine drainage and conduct research to obtain knowledge about optimal design characteristics three SRB reactors (II, III, and IV) with different attributes were designed. Two of the three reactors were placed below grade (ground) to minimize temperature changes and one above to study the effects of freezing. The reactors were filled with a combination of organic carbon, cobbles, and/or crushed limestone . Each reactor had a fifty foot section of cobble preceded by organic matter and/or limestone. Two of the three reactors had “pretreatment” sections, which consisted of an additional five foot section of organic carbon and a five foot section of crushed limestone; while the third one had only a five foot section of organic matter.

The most notable obstacle to the success was when the flow through reactor II ceased due to biofouling and consequent plugging. The problem was quickly addressed within a month.

The reactors were monitored monthly for sulfate, alkalinity, SRB count, heterotrophic bacteria count, dissolved oxygen, Eh (a measure of redox potential), and metals including: aluminum, zinc, cadmium, copper, iron, and manganese.

Overall, the results were positive, pH was increased and metals concentrations were reduced. Comparison of reactors shows that “initial increase of pH can largely be attributed to alkalinity present within the organic substrate rather than to limestone” (Zalusk, et al., 2000). Once SRB were established their metabolic reactions also contributed to pH increase.

Some of the more interesting findings when comparing the bioreactors included (Zalusk, et al., 2000):

- More organic matter leads to more organic matter fermentation reactions resulting in an increase in temperature; this could be critical in cold climates.

- Increased temperature leads to greater microbial activity.
- Prior to SRB activity, adsorption of metals to organic substrate seems to be the cause of concentration reductions.

B. Case Study: Champagne Creek - Butte, Idaho

The mine drainage from Moran Tunnel contributes low pH, metals-laden water discharging to Champagne Creek. The project is being handled through the Bureau of Land Management's Abandoned Mine Lands Program in the State of Idaho. The watershed is 9.2 square miles, moderately steep, at an elevation of 6060 feet, mostly covered by semi-arid rangeland. The stream itself is only 4.5 miles long, it is consumed by alfalfa hay irrigation and does not reach a receiving stream. The annual average precipitation is about 16 inches, the majority of runoff is due to snowmelt; in times of extreme drought the stream will run dry (Moore & Kotansky, 2002).

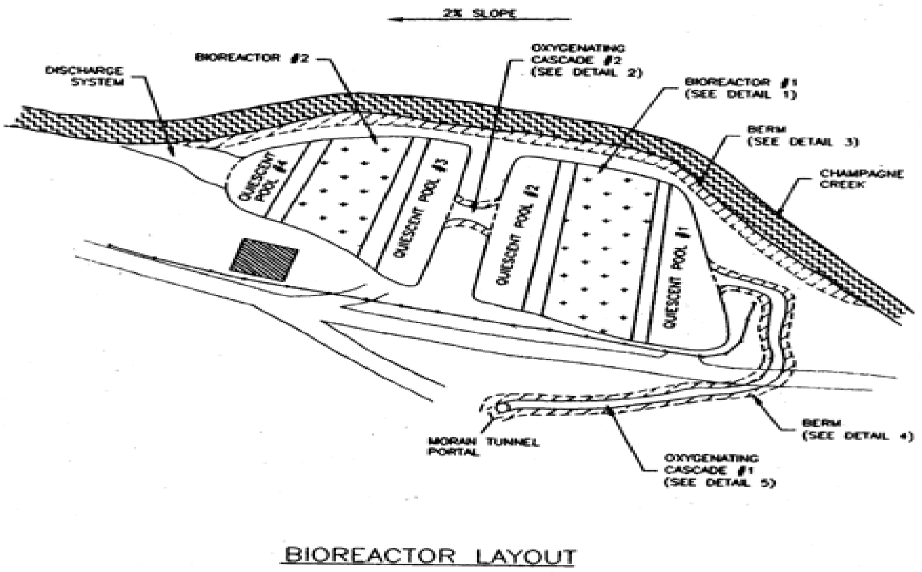

Figure 4. Schematic of Champagne Creek Bioreactor (Moore & Kotansky, 2002)

Mining around Champagne Creek began around 1883 with the discovery of silver ores, this first mine operation ended around 1887. In the late 1920s deeper base-metal sulfide ores were mined for lead and zinc. Around this same time the Moran Tunnel was constructed with the hope of intersecting the Last Chance vein at around 450 feet below the surface; the vein was never found. The area was last mined in 1946.

The site underwent a Preliminary Assessment in 1985 and a Site Investigation in 1988. The Bureau of Land Management completed its own study in 1989. It was this report that required additional water quality monitoring and a review of which passive treatment wetland system might be able to be used (Moore & Kotansky, 2002).

In 1999 cleanup at the Moran Tunnel began. The first actions were removal of waste rock piles, a 17,500 cubic yard pile was placed in a repository above the flood plain; additional waste rock totaling 2700 cubic yards from surrounding areas was also placed in this repository (Moore & Kotansky, 2002). A four-cell passive bioreactor system was constructed based on SRB and lime treatment. The cells consisted of organic material (manure and hay) to encourage SRB establishment and limestone to neutralized acidic discharges (Moore & Kotansky, 2002). Berms were also put into
place leading to the passive system; they were made up of lime and materials to encourage SRB growth.

The system was effective in improving water quality for the first few months of operation (S. Moore, personal communication, 7/30/2003). The pH from pond 1 to pond 2 increased from 3.3 to 6.4. The first winter (1999-2000) after installation revealed lower metal discharges and a decrease in SRB activity common during cold weather (Moore & Kotansky, 2002). The first berm, made of "limestone and SRBs," initially led to a decrease in aluminum and copper of nearly 100-percent, 92-percent of cadmium, 77-percent of zinc, and 65-percent of iron (Moore & Kotansky, 2002). By May 0f 2000 the removal rates were nearly 100-percent aluminum and copper, 91-percent iron, and 56-percent zinc (Moore & Kotansky, 2002).

In 2001 the passive treatment system was enhanced with the addition of an anaerobic treatment tank. It was added between the discharge from the Moran Tunnel and the first treatment pond. The tank was put into place because water quality data indicated that the high concentration of iron on the first pond was interfering with the effectiveness of the bioreactor berms in removing zinc, copper, and buffering pH (Moore & Kotansky, 2002). Eventually, the tank also clogged and performance of the system declined (S. Moore, personal communication, 7/30/2003).

The system has required recharge of the berms with "SRBs and limestone" and the addition of the anaerobic tank (Moore & Kotansky, 2002). This system has not yet proved to be a walk-away solution, but BLM-Idaho are working on improving the system and carefully documenting efforts so that lessons may be learned for future projects (S. Moore, personal communication, 7/30/2003).

2.2.4 Successive Alkalinity Producing Systems

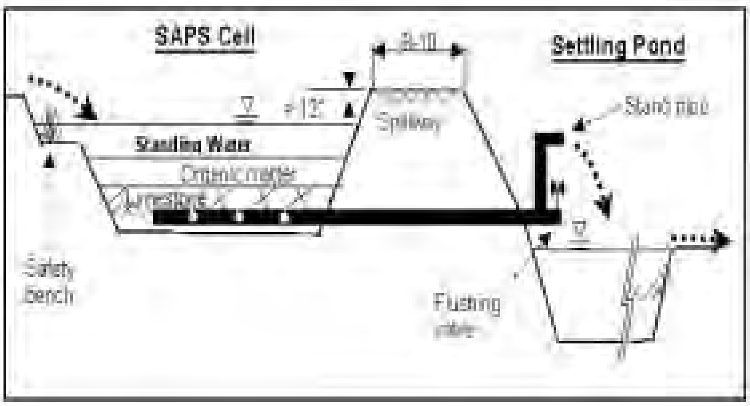

Figure 5. General Schematic of a SAPS Available at: http://sudan.cses.vt.edu/prp/Research_Results/SAPS.html

Successive Alkalinity Producing Systems have the following basic elements: organic mulch layer, limestone layer, and a drainage system - most include a flushing system as well. This technology was created in the early 1990's by Kepler and McCleary (Younger et al., 2002). The idea is that mine drainage flows into the tops of the cell creating a top layer of water which prevents the infiltration of oxygen into the bottom layers (water is also used in this way in tailings holding dams). The organic layer serves to remove dissolved oxygen from the water, farther down anaerobic conditions support the establishment of sulfate-reducing bacteria. The anaerobic environment is a reducing environment that changes Fe^{+3} to Fe,$^{+2}$ thereby reducing the likelihood of iron hydroxide precipitation, see equation 3. Since these units encourage reducing conditions and establishment of SRB, a major contribution to the treatment of the water, these units are sometimes referred to as RAPS - Reducing and Alkalinity Producing Systems (Younger et al, 2002). Finally, the water enters the limestone region, essentially devoid of oxygen preventing the armoring of limestone. Upon leaving the SAPS the water is usually directed to an aerobic settling pond or wetland to allow metals to form precipitates and further water polishing (Kepler & McCleary, 2003).

Many SAPS include flushing systems because as one would imagine oxidation and reduction of Fe and Al leads to precipitates that can clog the cell (Rees et al., 2001). The flushing systems generally operate by generating head differences that move water rapidly through the system (Kepler & McCleary, 2003).

SAPS tend to be more efficient than anaerobic wetlands and require less space to provide the same level of treatment (Younger et al., 2002). SAPS require some maintenance, not only for periodic flushing, but also to prevent or correct the development of preferential flow paths, possible in any of these passive systems (Kepler & McCleary, 2003; Rees et al., 2001). If preferential flow paths develop the water short circuits the system. They also require driving head and freeboard resulting in topographic relief requirements of greater than five meters (Younger et al., 2002).

A. Case Study: Oven Run, Pennsylvania

The watershed protection group Stoneycreek - Conemaugh River Improvement Project (SCRIP) located in western Pennsylvania, has initiated and completed multiple projects to improve their watershed. During a phone conversation with Dave , who is directly involved in this project, it was revealed that many of their remediation projects utilize SAPS (personal communication, 6/18/2003). Oven Run is one of the larger sites handled by SCRIP, it has six sources of highly acidic, metals-laden drainage totaling 720,000 gallons a day (Oven Run). Projected costs were $5 million, actual costs were $4.1 million (D. Steel, personal communication, 6/18/2003). Five of the six sources are treated using SAPS, the sixth has been backfilled. The first SAPS was installed in 1995, the last in 2003.

Figure 6. Oven Run, SAPS, Available at: http://www.ctcnet.net/scrip/stoven.htm

So far treatment has been successful in removing metals and acidity, while generating alkalinity. Not including the most recently installed SAPS, pH at downstream monitoring points have increased from the 3 to 4 range to the 5 to 6 range and 200 tons of iron and 200 tons of aluminum are removed each year. In addition, the samples showed some alkalinity, which is particularly impressive because other acidic waters drain into the creek after Oven Run, so the treated waters are able to buffer some of the additional pollution.

B. Case Study: #40 Gowen, Gaines Watershed. Oklahoma

This is a former coal mining site experiencing the typical aliments, acidity and elevated metals concentrations, mostly iron. This project was commissioned in 1998 with the help of an EPA Region 8 Section 319 grant and the Oklahoma Conservation Commission, by the University of Oklahoma (EPA, 2002c). This site, amongst other AMD sites, was designated as having the greatest impact on Pitt Creek, a

Figure 7. SAPS cell (“Section 319 Success Stories” Available at: http://www.epa.gov/owow/nps/Section319III/OK.htm

tributary to Gaines Creek which drains into Lake Eufaula (EPA 2002c). The Gaines Creek Watershed is located in Pittsburg and Latimer counties. The treatment design is a four-cell system with alternating vertical flow wetland (though figure shows little more than ornamental plant-life) and surface flow aerobic ponds. The project budget was $125,000 and was installed in 1998. To avoid confusion, the vertical flow cell is what would typically be defined as a SAPS though some define the entire alternating system as a SAPS as well. The vertical flow cell consists of a layer of water on top, followed by 1 meter of compost mixed with limestone and flyash and a cobble-fill pipe drainage system (EPA, 2002c).

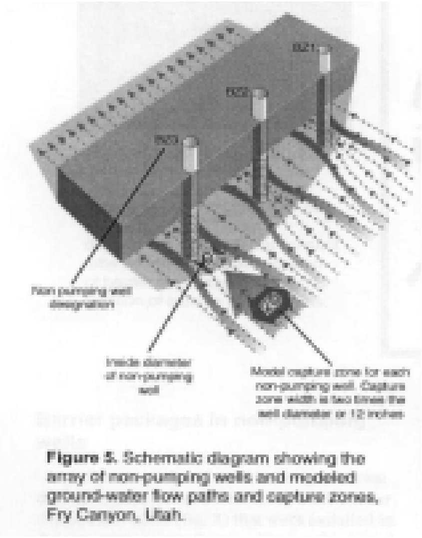

Figure 8. Schematic of Non-pumping well PRB.

There was not enough space at this site to construct a system that would be able to treat the entire flow; the system treats approximately 7600 gallons per day (EPA, 2002c). The design was based on “contaminant loadings of about 18,000 and 7,000 grams per day of acidity and iron” (EPA, 2002c). Removal rates for acidity are estimated to be 30 - 40 gram/meter^2 - day; the total surface area is approximately 750 meter^2.

The system has been in operation for two years and monitored every two weeks. Though actual data could not be obtained, the report about the project on EPA’s website indicates that “concentrations of iron, aluminum, and manganese have decreased significantly,” pH of the final effluent is at 6 and alkalinity is above 150 milligram/liter (EPA, 2002c). Trace metals - barium, cadmium, chromium, copper, nickel, zinc, and lead - were reduced to near or below detection levels. A recent biological survey counted 2000 healthy populations of fish and macroinvertebrates in three of four cells.

This project is of particular interest because it is the first successful passive treatment AMD treatment project carried out in Oklahoma (EPA, 2002c). The success of this project has spurred the state to use this wetland design at the Tar Creek Superfund site in Ottawa county, Oklahoma, and is being investigated for application in several watershed nationwide (EPA, 2002c).

2.2.5 Permeable Reactive Barriers

Permeable Reactive Barriers (PRBs) are exactly what they sound like: barriers that react with specific chemicals of concern that are placed in the path of groundwater flow allowing the water to flow through easily (Blowes et. al, 2000). In PRBs designed to treat acid mine drainage (AMD) with metals contamination the barrier is generally composed of solid organic matter, like municipal compost, leaf compost, and wood chips/sawdust (Blowes, et. al., 2000). Organic matter encourages the proliferation of sulfate-reducing bacteria that will reduce sulfate to sulfide and will result in the subsequent formation of insoluble metal sulfides which has been described with regards to bioreactors, please see equations 17 & 18. Research has been done to evaluate the efficiency of using PRBs to remove uranium contamination at abandoned mine sites; possible reactive materials are zero-valent iron, bone char phosphate, and amorphous ferric oxyhyroxide (Naftz, et al., 1999).

One important consideration in the design of a PRB to treat AMD is the stability of the metal sulfides (Blowes, et. al., 2000). Sulfides have low solubility in anaerobic conditions, if oxidation were to occur, metals could be released from their metal sulfide form into the environment (Blowes, et. al., 2000). An example of designing to prevent oxidation is illustrated by a project at Nickel Rim Mine, Sudbury, Ontario. The designers considered the implications of an oxidizing agent in the flow of groundwater and the PRB was covered by a 20cm saturated clay cap to prevent oxygen infiltration (Blowes, et. al., 2000).

Although not discussed much in this paper, former uranium mines are also a serious concern Naftz et al. conducted a field demonstration using six different PRBs to study the removal efficiencies of uranium at a site in southeastern Utah (1999). There were four different reactive media and two design types. Three of the PRBs were “funnel and gate” types, the gate is where the reactive media is located and the funnel is two impermeable walls directing groundwater to the gate. Each gate was consisted of a different material: (1) bone char phosphate (PO_4) pellets, the phosphate source facilitates the formation of insoluble uranyl phosphate compounds; (2) zero valent iron (ZVI) pellets which induce the reduction of uranium (VI) to the less soluble uranium (IV); and (3) pelletized amorphous ferric oxyhydroxides (AFO) which remove uranium by adsorption to the ferric oxide surface (Naftz et al., 1999). The other three PRBs were six-inch diameter non-pumping wells consisting of different proportions of bone char phosphate and foamed iron oxide pellets; the phosphate will adsorb to the iron pellets to allow access for formation of uranyl phosphate compounds (Naftz, et al., 1999). The hypothesis is that wells will allow for contact with deeper plumes and will be more suitable for remote locations (Naftz et al., 1999).

Results of the field demonstration were positive. After one year of operation and seven sampling events the funnel the ZVI barrier removed >99.9 percent consistently, the PO_4 barrier removed >90 percent on all but two of the seven sampling events, and the AFO barrier varied the most but still removed an average of 88.1 percent (Naftz, et al., 1999, Table 1). Data from the wells spans only three months and the results are not quite as impressive, but still reasonable; the average of removal rates overall was 67 percent (Naftz et al., 1999)

PRBs are a relatively new technology and work is continually being done to optimize installations. As it is often helpful to learn from past error a brief discussion of common problems of PRB performance is presented (Blowes, et. al., 2000).

1) Although barriers often have very long theoretical treatment lifetimes when only the material and the contaminants of concern are considered, actual lifetimes are considerably shorter due to the presence of other reactive substances in the environment;

2) Chemical reactions can be slowed due to depletion of reactive component of the barrier;

3) Precipitation of a secondary reactive precipitate can reduce the reactive surface area;

4) Physical clogging or preferential path flow.

2.2.6 Biosolids

Biosolids are treated municipal sewage sludge; the EPA defines biosolids as follows:

> "...the nutrient-rich organic materials resulting from the treatment of sewage sludge (the name for the solid, semisolid or liquid untreated residue generated during the treatment of domestic sewage in a treatment facility). When treated and processed, sewage sludge becomes biosolids which can be safely recycled and applied as fertilizer to sustainably improve and maintain productive soils and stimulate plant growth."

Biosolids have a growing number of useful applications and the search for more continues as population and hence sludge production increases. Biosolids are being used to reclaim mine lands (Murray et al., 1981; Sopper, 1993; Toffey, 2003) and have also been used for agricultural purposes. There are federal standards, namely Section 103C of the Clean Water Act and state standards that have to be met in order to apply biosolids to land. Over a twenty-five year period, the field experience with biosolids continues to demonstrate clear environmental benefits and negligible adverse effects (Sopper, 1993; EPA; Toffey, 2003).

When reclaiming mine sites biosolids are almost always applied with lime, either pre-mixed or in stages (R. Bastian, personal communication, 6/2/2003). Lime serves to increase the pH of the soil rapidly. Lime application alone may not be sufficient for long term improvement in the soil characteristics because the pH will eventually decline as sulfur-bearing minerals are oxidized (Sopper, 1993). However, biosolids application without lime has in some cases raised the soil pH and decreased availability of metals (Sopper, 1993).

Biosolids also show advantages over chemical fertilizers (Sopper, 1993) because they provide a source of carbon and capacity for moisture retention which are conducive to microbial and plant growth. This is important for the establishment of a long-term self-sustaining system. Sopper summarizes that biosolids application re-establishes a functioning microbial population comparable to undisturbed levels within two or three years of application, much more quickly than with traditional chemical treatment (1993).

The application of biosolids does not necessarily reduce the amount of metals present in the soil. In a draft report for the EPA, Maxemchuk explains that tailings sites treated with biosolids do not experience a reduction in total metals, rather metals availability is reduced (2001). Metals are immobilized through precipitation as carbonates, phosphates, sulfides, silicates and sorption by organic matter, and hydroxides (Sopper, 1993). In some cases vegetation may be responsible for immobilizing the metals, or might even remove the metals from the soil, also known as phyto-extraction.

There is ample evidence to support the use of biosolids in reclaiming mine lands. It is a cost-efficient method for reducing potential harm to the environment and its occupants. It is particularly attractive when the other options are removal and/or capping. Removal is generally expensive, especially when sites are very large and this approach just relocates the waste material, posing a potential problem at a new location. Capping alone can prevent further exacerbation of the problem, but will not help to re-establish a functioning ecosystem at the site unless natural soils are used. The use of natural soils as caps on large area sites is impractical, expensive and leaves "borrowed" areas highly disturbed and subject to intense erosion. Biosolids provide an apparently indefinite solution to contaminated sites because metals of concern are complexed, reducing their bioavailability, and the health of the A-horizon in the soil profile is improved. This allows vegetation to replenish itself - stabilizing and improving the health of the ecosystem in the area.

A. Case Study: Frostburg, Maryland

This project is a testament to the longevity of the use of biosolids in the reclamation of mine lands. The field plot experiments were installed in 1974 on a former strip mine. The site had been completely devoid of vegetation for four years (Griebel et al., 1979). The overburden and rock wastes resulted in a dark-colored, acidic - pH of 2.9, spoil material (Griebel et al., 1979).

A total of nine test plots 3.6m x 4.5m were installed. There were three basic applications tested: biosolid compost alone, biosolid compost with rock phosphate, and biosolid compost with dolomitic limestone (Griebel et al., 1979). For each of these three scenarios biosolids were applied in three different amounts: 56 metric tons per hectare (mt/ha), 112 mt/ha, and 224 mt/ha (Griebel et al., 1979). The biosolids were supplied by the Blue Plains Wastewater Treatment Plant in Washington, DC. They were then composted at ARS-MES Composting Facility in Beltsville, Maryland. When sewage sludge is composted the material becomes more humus-like and excess heat and water are driven off and decreases in the availability of certain metals results (Griebel et al., 1979). Both rock phosphate and dolomitic limestone were applied at the rate of 11 mt/ha. In addition, each plot received 110 kg/ha of nitrogen in the form of NH_4NO_3. A grass legume seed mixture was applied at 40 kg/ha and Empire birdsfoot trefoil, *Lotus Coniculatus L.*, was applied at 10 kg/ha (Griebel et al., 1979)

After two years the vegetation was harvested and analyzed for yield and metals uptake into the plants. Soil conditions were also analyzed.

After two years the control plot had a pH of 3.1, the test plots had pH's as seen in the table below. The plots with the maximum biosolid application had the most improved pH; interestingly the difference between compost alone and compost with alkaline amendments did not differ significantly.

pH of the Soil Two Years After Biosolids Application

	56 mt/ha of biosolid	112 mt/ha of biosolid	224 mt/ha of biosolid
compost alone	4.2	3.9	5.0
compost & rock phosphate	4.5	4.8	5.1
compost & dolomitic limestone	4.6	4.8	5.1

Adapted from Griebel et al., 1979

Plant yields, shown in figure 9, below are from a single harvest taken during the second growth season (Griebel et al., 1979). Overall the results are positive, and certainly better than the control plot with no amendments.

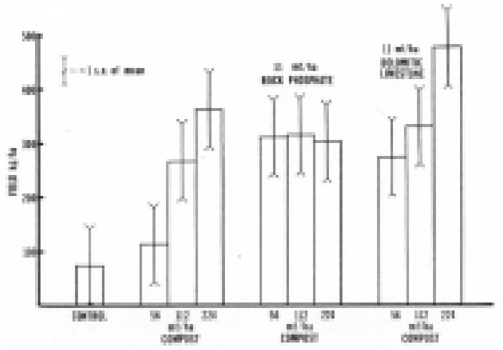

Figure 25-1. Forage yields (tall fescue and birdsfoot trefoil) produced on an acid strip mine spoil amended with sewage sludge compost, rock phosphate, and dolomitic limestone

Figure 9. Plant biomass yields two years after biosolids application (Griebel et al., 1979, figure 25-1)

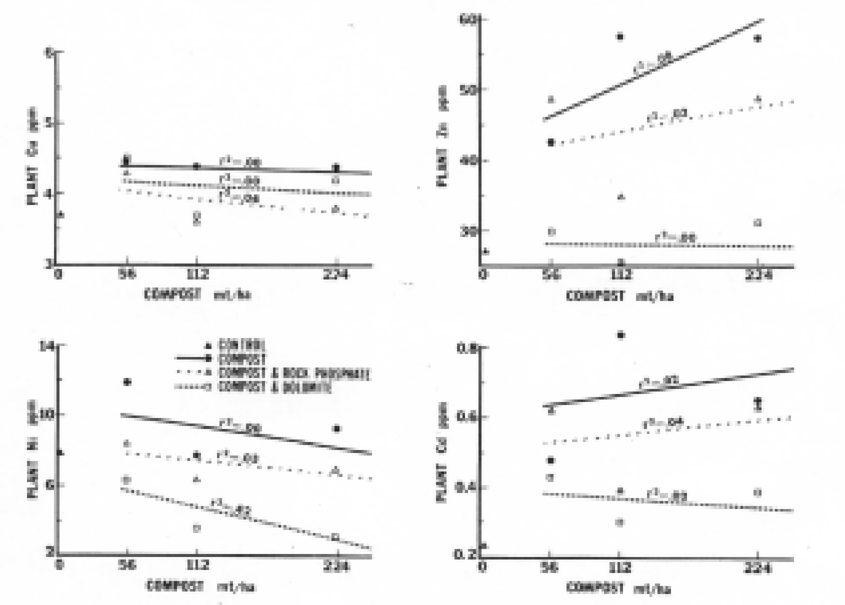

Figure 10. Relationship between total plant metals and rates of application of biosolids and other amendments (Griebel et al., 1979, figure 25.8)

One of the more interesting things to note is that the "lowest compost treatment (56 mt/ha), used in combination with either rock phosphate or dolomite, provides yields equal to those obtained with 112 mt/ha compost alone" (Griebel et al., 1979. p. 296). Furthermore, the highest rate of compost alone (224 mt/ha) was exceeded only when the same amount was applied with dolomitic limestone (Griebel et al., 1979).

A common concern when applying biosolids at metals contaminated sites with the intention of establishing vegetation is that the vegetation will accumulate high levels of metals that could potentially be a hazard to wildlife. In this study the observed metal concentrations of Cu, Zn, Ni, and Cd in vegetation were well within the range of concentrations found in vegetation produced on regular agricultural soils (Griebel et al., 1979). Figure x shows the concentrations of the metals with respect to each amendment combination. It is obvious from studying the graphs that the addition of limestone or phosphate rock reduces the amount of metals taken up by the plants, generally to around the levels found in the control plot's vegetation.

B. Case Study: Leadville, Colorado

Biosolids were applied at the Leadville site to revegetate the alluvial tailings deposits that were washed in and around the Arkansas River. The tailings have been deposited at various locations along an 11-mile stretch of the river. This has created a variety of environmental problems including acidic soils in the range of pH 1.5-4.5, Zn and Pb salt formation on the soil surface, sedimentation in the river of up to two feet in some spots, and death of vegetation leading to erosion of river banks ("Upper Arkansas," 2000).

Figure 11. Metal salt accumulation on soils in Leadville, CO on the banks of the Arkansas River, (Upper Arkansas, 2000).

Biosolids provided by Denver Metro were applied to portions of the site at a rate of 100 dry tons/acre in August of 1998 ("Upper Arkansas," 2000). Approximately 100 tons/ac of lime were also applied; both were tilled into the soil at a depth of twelve inches ("Upper Arkansas," 2000). A variety of soil amendment combinations were also applied to test plots at the site, to determine which mix of biosolids and alkaline agent would promote the most vegetation. During a visit to the site in July of 2003 it appeared that the applications were working quite well.

2.2.7 Phytoremediation

Phytoremediation suggests the use of plants to treat or remove contamination. Wong defines the term as, "the use of green plants and their associated microbiota, soil amendments, and agronomic techniques to remove, contain, or render harmless environmental contaminants (2003). Though there are a wide variety of subcategories in the field of phytoremediation only four will be discussed in this paper, phytoextraction/phtyomining, phytostabilization, rhizofiltration, and phytovolatilization. For more information about other technologies, consult US EPA's Introduction to Phytoremediation.

Phytoextraction, or phytomining if metals can be recovered, is defined as:

> "the uptake of contaminants by plant roots and translocation within the plants. This concentration technology leaves a much smaller mass to be disposed of than does excavation of the soil or other media" (EPA, 2000, p. 143).

There are a limited number of plants known to be capable of this and climate determines what species can be used. Phyto-mining requires that the plants be "hyperaccumulators," i.e., they will uptake more than the average concentration of metals. According to Brooks et al., there are about 300 species that hyperaccumulate nickel, 26 cobalt, 24 copper, 19 selenium, 16 zinc, 11 manganese, one thallium and one cadmium (1998). Although these numbers are encouraging there are few field applications. An important consideration in applying phytoextraction, especially with the use of hyperaccumulators, is whether the resulting vegetation will be hazardous to local animals; this possibility varies from site to site (Wong, 2003).

Phytostabilization is fairly common with regards to mining sites, it is a common practice to revegetate spoiled mine lands to prevent soil erosion and deposition of contaminated soils in streams and nearby lands. The EPA defines it as:

> "(1) immobilization of a contaminant in soil through adsorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants, and (2) the use of plants and plant roots to prevent contaminant migration via wind and water erosion, leaching, and soil dispersion" (EPA, 2000, p. 21).

Ideal plants for this technique use metal-tolerant, drought-resistant, fast growing crops that can also grow in nutrient deficient soils (Wong, 2003). The advantages are that it is a relatively inexpensive technique, soils do not need to be removed, ecosystem restoration is enhanced, and disposal of hazardous materials or biomass is not required (EPA, 2000). Disadvantages are that the contaminants remain in place - care must be taken to ensure that the vegetation continues to stabilize the metals; extensive fertilization or soil modification may be necessary; plant uptake and translocation of metals must be prevented; root zones, root exudates, contaminants, and soil amendments must be monitored to prevent an increase in metal solubility and leaching; it may only be considered a temporary measure; stabilization might be due primarily to the effects of soil amendments, with plants only contributing to stabilization by decreasing the amount of water moving through the soil and by physically stabilizing the soil against erosion (EPA, 2000). The application of biosolids fits well with this phytoremediation technique as it provides necessary fertilizing agents and aids in microorganism establishment.

Rhyzofiltration involves the removal of contaminants in solution through adsorption or precipitation onto plant roots or absorption into the roots, this can also be achieved by the microorganisms associated with the rhizosphere (EPA, 2000; Wong, 2003). This technology is applied in water, that is the plants are either aquatic plants or terrestrial plants on a floating platform (EPA, 2000). Contaminants can be physically removed by removing the plants themselves. Some of the disadvantages to this technology include a need for good control over pH, and a clear understanding of the chemical speciation and interaction of all species in the influent (EPA, 2000). In addition to this, control over influent concentration and flow rate may be necessary, plants may need to be grown and then translocated to the site (especially terrestrial plants), periodic harvesting and disposal are required, and laboratory results might not be achievable in the field (EPA, 2000). Phytovolatilization has been identified as a potential treatment for mercury and selenium contaminated soils (Chaney, et al., 1997; EPA, 2000). Phytovolatilization is defined by the EPA as,

> "...uptake and transpiration of a contaminant by plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant through contaminant uptake, plant metabolism, and plant transportation" (EPA, 2000).

This process is beneficial if the contaminants of concern will be transformed to less-toxic forms, for example elemental mercury and dimethyl selenite gas. The disadvantages are uncertainty about metabolites, unhealthy plant accumulation, and uncertainty about other constituents at the site, i.e., where there is one form of contamination there could be many more and one must understand how they will react with the plants as well. For more information including references and plant species appropriate for the different technologies discussed here please see the following reference: Introduction to Phytoremediation, 2000; Wong, 2003; Brooks et al., 1998; Brooks, 1998; and, Madejon et al., 2003.

3.0 Conclusion

Given the seriousness and scale of mine drainage it is important to continue to work towards affordable and effective treatment options. The passive treatments discussed in this paper are exhibiting mixed success, results are encouraging but not the “walk-away,” cheap solution that they are sometimes described to be. Still the innovative treatments discussed here are showing progress and with further research and performance analysis these technologies may become more widely used in the future. While there are drawbacks to traditional treatments, there are some benefits that make them widespread and in some cases the preferred alternative.

As with almost any topic, there is need for more work, some of the more pressing areas include communication, funding, and research about fundamental processes that cause precipitation of metals. Many of the people contacted for this report expressed their desire for a better line of communication and access to information about similar projects. The database created in conjunction with this report began to create a place to access project information, though it is not a complete picture of the efforts being done. Regional communication between parties working with similar geology and climate would probably be the most useful effort as the performance of passive treatments seems to be greatly affected by these factors. Funding, or lack thereof, is a serious issue especially for hard rock sites. As previously mentioned, non-coal states are not eligible for SMCRA funds and states that are eligible must address coal-related issues before hard rock. Considering the number of hard rock sites it does not seem reasonable to rely on existing federal and state environmental funds, for example CERCLA and CWA, to sponsor remediation efforts. As mentioned earlier in this paper, some states are making efforts to identify and remedy this funding problem. Research about the precipitation of metals has been done, however, the differences from site to site in geology, hydrology, climate, and chemistry make general application of this information quite difficult. Each site must be addressed separately to account for the variations that occur in nature. As experience builds and information is shared the application of passive technologies will improve.

4.0 References

Bastian, Robert (EPA-Office of Solid Waste and Emergency Response). Personal communication. 2 June 2003.

Blowes, David W., Ptacek, Carol J, Benner, Shawn G., McRae, Che, Bennett, Timothy A., & Puls, Robert W. (2000) Treatment of inorganic contaminants using permeable reactive barriers. Journal of Contaminant Hydrology, 45 (1-2), 123-137.

Brooks, R. R. (ed.) (1998). Plants that hyperaccumulate metals their role in phytoremediation, microbiology, archaeology, mineral exploration, and phytominig. CAB International: 1998.

Brooks, Robert R. Chambers, Michael F., Nicks, Larry J., and Robinson, Brett H. (1998) Phytomining. Trends in Plant Science, 3 (9), 359-362.

Chaney, Rufus L., Malik, Minnie, Li, Yin M., Brown, Salley, Brewer, Eric P., Angle, J. Scott, and Baker, Alan JM. (1997). Phytoremediation of soil metals. Current Opinion in Biotechnolgoy, 8 (3), 279-284.

Cravotta, Charles A. & Watzlat, George R. (2002) "Design and Performance of Limestone Drains to Increase pH and Remove Metals From Acid Mine Drainage." In: Handbook of Groundwater Remediation Using Permeable Reactive Barriers: applications to radionuclides, trace metals, and nutrients. (See Naftz, et. al. 2002 below).

Dempsey, Brian A. & Jeon, Byong-Hun. (2001) Characteristics of sludge produced from passive treatment of mine drainage. Geochemistry: Exploration, Environment, Analysis, 1, 89-94.

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Forba, Russ (EPA-Region 8). Personal communication. 20 June, 2003.

Griebel, George, E., Arminger, Walter H., Parr, James, E., Steck, D.W., and Adam, J.A.. (1979). "Use of Composted Sewage Sludge in Revegetation of Surface-Mined Areas." Utilization of Municipal Sewage Sludge Effluent and Sludge on Forest and Disturbed Land. Sopper, William E. and Kerr, Sonja, N. (eds.) Pennsylvania: The Penn State University Press.

Gusek, James, J. and Wildeman, Dr. Thomas R (1995). New Developments in Passive Treatment of Acid Rock Drainage. This article is from the South African Mining Delegation Seminar. Denver, CO, USA. Aug. 24 - Sept. 4, 1998. (First presentated at: Engineering Foundation Conference on Technical Solutions For Pollution Prevention in the Mining & Mineral Processing Industries, Palm Coast, Florida. Jan 22-27 1995.)

Gusek, James J. (1996). Passive Treatment of Acid Rock Drainage: What is the Potential Bottom Line? International Journal of Rock Mechanics and Mining Science & Geomechanics Abstracts, 33, (2) 95A.

Gusek, James J. (1998). (Knight Piesold, LLC; 1050 Seventeenth St., Suite 500; Denver, CO 80265-0500). Three Case Histories of Passive Treatment of Metal Mine Drainage. This article is from the South African Mining Delegation Seminar. Denver, CO, USA. Aug. 24 - Sept. 4, 1998.

Hedin, Robert S., Narin, Robert W., Kleinmann, Robert L. P. (1994). Passive Treatment of Coal Mine Drainage. Bureau of Land Mines Information Circular 9389.

Holmes, Michael. (EPA-Region 8). Personal communication. 22 July, 2003.

Hopey, Don. (2001, August 10). Seeing Red and Profit from Mine Iron Oxide Touted for Paint, Hair Dye. Pittsburgh Post – Gazette. pp. B-4.

Kepler, D. & McCleary, E. (Damariscotta). (2003). Successive Alkalinity Producing Systems - for the 2003 West Virginia Surface Mine Drainage Task Force Symposium. Available at: http://www.wvu.edu/~agexten/landrec/2003TFS/Kepler03.pdf.

Lauzon, Shelly (Woods Hole Oceanographic Institution). (2002, March). New Iron Eating Microbe Major Component of Mining Pollution and Iron and Sulfur Cycling. Available at: http://www.whoi.edu/media/IronEatingMicrobe.html

Lewis, Jim (Colorado Department of Public Health and Environment). Personal communication. 16 July, 2003.

Macalady, Donald L. (Ed.). (1998) Passive Bioremediation of Metals and Inorganic Contaminants. Perspectives in Environmental Chemistry. New York: Oxford University Press. p 473-495.

Madejon, P., Murillo, J. M., Maranon, T, Cabrera, F, and Soriano, M.A. (2003, May) Trace elements and nutrient accumulation in sunflower plants two years after the Aznalcollar mine spill. The Science of the Total Environment, 307. (1-3) pp. 239-257.

Welch, E. B. (1980). Ecological Effects of Waste Water. New York, NY: Cambridge University Press.

Matlock, Matthew M., Howerton, Brock S., & Atwood, David A. (2002). Chemical Precipitation of heavy metals from acid mine drainage. Water Research 36, 4757-4764.

Matlock, Matthew M., Howerton, Brock S., & Atwood, David A. (2003). Irreversible binding of mercury from contaminated soil. Advances in Environmental Research 7, 347-352.

Matlock, Matthew M., Howerton, Brock, S., Aelstyn, Michael Van, Henke, Kevin, R, and Atwood, David A. (2003). Soft metal preferences of 1,3-benzenediamidoethanethiol. Water Research, 37, 579-584.

Maxemchuk, Amanda. (2002). DRAFT of Final Report: Assessment of Ecological Risk From Untreated Mine Tailings and the California Gulch Superfund Site in Leadville, Colorado, Phase IV: August 2001 Sampling Event. [Prepared for Harry Compton & Mark Sprenger of EPA].

Mineral Policy Center. (2003). Cleaning Up Abandoned Hardrock Mines. Available at: http://www.mineralpolicy.org/us/abandoned.php

Moore, Steve. (Bureau of Land Management). Personal communication. 30 July, 2003.

Moore, Steve and Kotansky, Dan (US Dept. of the Interior, Bureau of Land Managment, Abandoned Mine Lands, Idaho) (Feb. 2002). AML Project Notebook: Project Name: Champagne Creek Restoration. Available at: http://www.id.blm.gov/aml/projects/champagne/index.htm

Murry, Douglas T., Townsend, Steven A., and Sopper, William E. (1981) Using Sludge to Reclaim Mineland. BioCycle, 22 (3), 48-55.

Naftz, David L., Morrison. Stan J., Davis, James A., & Fulter, Christopher (Eds.). (2002). Handbook of Groundwater Remediation Using Permeable Reactive Barriers: applications to radionuclides, trace metals, and nutrients. San Diego, California: Academic Press. [ISBN: 0-12-513563-7]

Naftz, David L., Davis, J.A., Fuller, C.C., Morrison, S.J., Freethey, G.W., Feltcom, R.G., Wilhelm, M.J., Piana, J. Joye, and Rowland, R.C. (1999). *Field Demonstration of Permeable Reactive Barriers to Control Radionuclide and Trace-Element Contamination in Ground Water from Abandoned Mine Lands*. U.S. Geological Survey Toxic Substances Hydrology Program - Proceedings of the Technical Meeting, Charleston, South Caroline, March 8 -12. USGS Water Resources Investigations Report 99-4018A, Volume 1, Contamination from Hard-Rock Mining. Available at: http://toxics.usgs.gov/pubs/wri99-4018/

Nash, J. Thomas (2002). Hydrogeochemical Investigations of Historic Mining Districts, Central Western Slope of Colorado, Including Influence on Surface-Water Quality. U.S. Dept. of the Interior: U.S. Geological Survey. USGS Digital Data Series DDS-73 Version 1.0. Available at: http://pubs.usgs.gov/dds/2002/dds-073/dds-073.pdf

Nuttall, Charlotte A., Younger, Paul L. Zinc removal from hard, circum-neutral mine waters using a novel closed-bed limestone reactor. Water Research, 34 1262-1268.

Oklahoma Department of Environmental Quality. Governor Frank Keating's Tar Creek Superfund Task Force, Water Quality Subcommittee Task 2 Report, Water Quality Improvement Alternatives. (2000, Sept. 7). Available at: http://www.deq.state.ok.us/LPDnew/Tarcreek/WQTask2FinalReport.PDF

Oven Run Project: Project Key to Making Stonycreek a Net Alkaline System. Available at: http://www.ctcnet.net/scrip/stoven.htm

Pioneer Technical Services, Inc. (2002). Draft Final Expanded Engineering Evaluation/Cost Analysis(EEE/CA) For the McLaren Tailings Site; Cooke City, Montana. Prepared for: Mr. John Koerth, Montana Dept. of Environmental Quality - Mine Waste Cleanup Bureau. http://www.deq.state.mt.us/Rem/mwc/download.asp

Rees, Ben., Bowell, Rob, Dey, Matt, & Williams, Keith. (2001). Performance of a Successive Alkalinity Producing System (SAPS). Available at: http://www.srk.co.uk/news/SAPS_Manuscript.pdf

Sasowsky, Ira D., Foos, Annabelle, & Miller, Christopher M. (2000). Lithic controls on the removal of iron and remediation of acidic mine drainage. Water Research, 34. (10) pp. 2742-2746.

Sopper, William E. (1993). Municipal Sludge Use in Land Reclamation. Lewis Publishers: Boca Raton.

Steele, Dave (District Manager of Somerset County Conservation District). Personal communication. 18 June. 2003.

Stephens, James F., Rogers, Robert S., Fields, Phillip K. (2001, March) Conservation Practices for the Reclamation of Surface Mines in Arkansas. Arkansas Department of Environmental Quality, Surface Mining and Reclamation Division. Available at: http://www.adeq.state.ar.us/mining/pdfs/handbook.pdf

Successive Alkalinity Producing Systems for Renovation of Acid Mine Drainage. [associated with Virginia Tech, Powell River Project]. Available at: http://sudan.cses.vt.edu/prp/Research_Results/SAPS.html

Toffey, William. (2003) Twenty-five Year of Mine Reclamation with Biosolids in Pennsylvania. From Conference Proceedings : RevTech: Cleaning Up Contaminated Properties for Reuse and Revitalization: Effective Technical Approaches and Tools, USEPA Technology Innovation Office. July 22-24, 2003. Marriott City Center, Pittsburgh, PA.

Upper Arkansas River Alluvium Remediation: Biosolids Demonstration, Leadville, CO (2000). Available at : http://faculty.washington.edu/clh/leadville.html

U.S. Department of the Interior (2002a) : Office of Surface Mining. Abandoned Mine Land Program. Unreclaimed Problems: Public Health & Safety Coal Related High Priority Problems (Priority 1 & 2). Available at: http://www.osmre.gov/aml/remain/zintroun.htm.

U.S. Department of the Interior (2002b) : Office of Surface Mining. Acid Mine Drainage Treatment Techniques and Costs. Available at : http://www.osmre.gov/amdtcst.htm

U.S. Department of the Interior (2003a) : Office of Surface Mining Reclamation and Enforcement. White paper on: "People Potentially at Risk From Priority 1 & 2 AML Hazards" Available: http://www.osmre.gov/pdf/wp041703.pdf

U.S. Department of the Interior (2003b) : Bureau of Land Management: Abandoned Mine Lands Cleanup Program. Frequently Asked Questions. Available at: http://www.blm.gov/aml/faqs.htm

U.S. General Accounting Office. (1996). Federal Land Management: Information on Efforts to Inventory Abandoned Hard Rock Mines. Washington, DC. Available at: http://frwebgate.access.gpo.gov/cgi-bin/useftp.cgi?IPaddress=162.140.64.21&filename=rc96030.pdf&directory=/diskb/wais/data/gao

U.S. Environmental Protection Agency (1993a). [Wildeman, Thomas, Dietz, John, Gusek, James, Morea, Susan.] Colorado School of Mines - Constructed Wetland-Based Treatment. EPA/540/R-93/523. Full Report available at: http://www.epa.gov/ORD/SITE/reports.html.

U.S. Environmental Protection Agency. (1993b). Emerging Technology Summary: Handbook for Constructed Wetlands Receiving Acid Mine Drainage. EPA/540/SR-93/523.

U.S. Environmental Protection Agency (1999). Review of Passive Systems for Treatment of Acid Mine Drainage: MEND (Mine Environment Neutral Drainage Program) Report 3.14.1. May 1996: revised 1999. Available at: http://www.epa.gov/NE/superfund/sites/elizmine/43547mend.pdf

U.S. Environmental Protection Agency (2000), National Risk Management Research Laboratory, Office of Research and Development. Introduction to Phytoremediation. EPA/600/R-99/107.

U.S. Environmental Protection Agency: Solid Waste and Emergency Response. (2001). Abandoned Mine Site Characterization and Cleanup Handbook. EPA530-R-01-002.

U.S. Environmental Protection Agency (2002a). Biosolids. Available at: http://www.epa.gov/owm/mtb/biosolids/index.htm

U.S. Environmental Protection Agency (2002b). SITE Technology Capsule: Anaerobic Compost Constructed Wetlands Technology. EPA/540/R-02/506a.

U.S. Environmental Protection Agency (2002c). Section 319 Success Stories, Vol. III: Acid Mine Drainage Treatment Wetlands: A Sustainable Solution for Abandoned Mine Problems. Available at: http://www.epa.gov/owow/nps/Section319III/OK.htm

U.S. Environmental Protection Agency (2003). Active NPL Sites: California Gulch. Available at: http://www.epa.gov/region8/superfund/sites/co/calgulch.html

U.S. Environmental Protection Agency. A Handbook of Constructed Wetlands: Volume 4 Coal Mine Drainage. 843F00003. [Search for document title or number at http://www.epa.gov/clariton/clhtml/pubtitleOW.html]

Wong, M.H. (2003) Ecological Restoration of Mine Dredged Soils, With Emphasis On Metal Contaminated Soils. Chemosphere Issue 6, 775-780.

Younger, Paul, Banwart, Steven A, Hedin, Robert, S. (2002) Mine Water: Hydrology, Pollution, Remediation. The Netherlands: Kluwer Academic Press.

Zaluski, Marek, Trudnowski, John, Canty, Marietta, Baker, Mary Ann Harrington (MSE Technology Applications, Inc. Butte, Montana). Performance of Field-Bioreactors with Sulfate-Reducing Bacteria to Control Acid Mine Drainage. Fifth International Conference on Acid Rock Drainage, 20-26 May, 2000, Denver, CO Society for Mining, Metallurgy, and Exploration, Inc. (SME), Littleton, CO. ISBN: 0-87335-182-7. Vol 2, p 1169-1175.

Appendix A: State Mine Reclamation/Remediation Status

This section presents state programs and activities that address abandoned mines. The focus was limited to Western states dealing with hard rock mines. Note that this list is not comprehensive of all of the programs and activities occurring in each state.

Alaska

Department of Natural Resources
Division of Mining, Land & Water
http://www.dnr.state.ak.us/mlw/mining/aml.htm

Funding for this program comes from SMCRA funds. The state is only able to generate $200,000, but has $2 million in reclamation needs; therefore, the state qualifies for Minimum Program Status from the SMCRA fund, entitling them to $1.5 million plus emergency funds annually until the work remaining on the inventory drops below $2 million.

Coal and non-coal mining abandoned mines were inventoried. The coal inventory is complete, and 340 sites were identified. The non-coal inventory is incomplete with a count of 432. Each site was evaluated to determine funding eligibility. Priority 1 and 2 coal projects must be completed first, so only priority non-coal projects can be reclaimed. Priority 3 projects can be worked on in conjunction with Priority 1 and 2 projects or after all Priority 1 and 2 projects have been completed.

The state developed a variety of priorities to select sites for remediation; they came up with 224 coal projects and 32 - 123 non-coal projects. Initial inventories estimated costs at $52 million and non-coal costs at $2.7 million. To date, 36 AML projects have been completed at a cost of $8,880,980. Most of the projects involved preventing physical hazards.

U.S. Department of the Interior - Bureau of Land Management - Alaska
http://www.ak.blm.gov
http://www.ak.blm.gov/amines/amlindex.html

About 15 to 20 projects are either active or have been completed. Projects are selected using water shed approach (i.e., projects that will have the greatest impact on water quality in the watershed are chosen first). As with many of the programs, funding is an issue. The Web page states, “Because there is never enough money, the BLM must first consider watersheds damaged by abandoned mines.”

Arizona

Arizona State Mine Inspector

http://www.asmi.state.az.us

http://www.asmi.state.az.us/abandoned.html

Part of this state office's mission is to review and monitor all mine reclamation activities. This office established the Abandoned and Inactive Mine (AIM) Survey to inventory abandoned and inactive mines throughout Arizona. The majority of the funding for this program comes from the Bureau of Land Management. The program began inventorying sites in 1992 and estimates that there are at least 125,000 abandoned or inactive openings in the State of Arizona.

As of January 1999, 7,844 mines have been surveyed, with 288 mines with some type of Environmental Hazards and 1149 mines with Significant Public Hazards.

U.S. Department of the Interior - Bureau of Land Management - Arizona

http://www.az.blm.gov/

California

U.S. Department of the Interior - Bureau of Land Management - California

http://www.ca.blm.gov

http://www.ca.blm.gov/pa/aml/ - for specific AML activity

The California BLM manages 15 Resource Areas (RA's, Field Offices) comprising over 16 million acres in California and Northwest Nevada. Over 12,000 mine properties in California and Northwest Nevada are listed in the Bureau of Land Mines Mineral Industries Location System (MILS) database as on BLM land. An estimated additional 5000 sites likely to be on BLM land are not recorded in this database are. Of these 17,000 sites, an estimated 3000 significant properties contain hazardous substances or physical features and/or have environmental problems. No comprehensive AML inventory has been conducted on any RA in the state and six RA's have no recorded inventory of mine sites.

"The California State Office, (with limited staff) from mid-2000, has been conducting watershed-based projects that have and will continue to identify mine sites with environmental and/or safety issues" (http://www.ca.blm.gov/pa/aml/). To date about 40 sites have been identified as "high priority," more than 170 sites have been added to the Abandoned Mine Land Identification System - a database of AMLs on BLM lands. According to the website 7 projects have been completed as of April 21, 2003.

California Environmental Protection Agency

State Water Resources Control Board

http://www.swrcb.ca.gov/

One of the things found via this website was a document entitled, "The Abandoned Mine Technical Advisory Committee's Report on Abandoned Mines." [http://www.swrcb.ca.gov/nps/docs/tac_abandmin.doc] The document was created by the Abandoned Mines Technical Advisory Committee (TAC). TAC spent six months discussing the issues surrounding abandoned mines, past cleanup efforts, and desired future courses of action. They prioritized courses of action and identified barriers to progress. TAC identified lack of funding as a key impediment to cleanup of abandoned mines.

California is not a coal-mining state and therefore is ineligible to receive SMCRA funds.

Colorado

Colorado Department of Public Health and Environment

Hazardous Materials and Waste Division

http://www.cdphe.state.co.us/hm/hmhom.asp

This division regulates solid waste management, treatment, disposal facilities, and hazardous waste generation, storage, transportation, treatment, and disposal. The division also ensures compliance with state hazardous waste regulations and permits and oversees remediation of contamination at Federal Facilities located in the state. The division assists in the cleanup of hazardous waste sites under the Superfund Program, and encourages brownfields redevelopment through implementation of the Voluntary Cleanup and Redevelopment Act.

This state agency has dealt with the remediation of a few mine sites including Bonanza, Clear Creek, Eagle, Idarado, Leadville (California Gulch), and Summitville Mine.

U.S. Department of the Interior - Bureau of Land Management

Colorado Abandoned Mine Land Program

http://www.co.blm.gov/mines/mine.htm

There are about 2,600 abandoned mines on Colorado's public lands. The projects during 2002 are listed below. The projects are being addressed with a watershed approach.

Arkansas Watershed:

    LakeFork Project - includes Nelson and Dinero Tunnel Projects
    Mill Sap Gulch Project
    Mount Robinson Project/Historic Rosita Mining District

Upper Animas Watershed

    Elk Tunnel
    Forest Queen
    Joe and John
    Lackawanna and Lark
Upper Gunnison Watershed
    Palmetto Mine Remediation
    Roy Pray #1 Remediation
    Ute Ulay Mine/Mill Remediation and Mine Waste Repository
    Wyoming Mine Remediation

Many of the project involve water diversion, materials removal, and revegetation.

United States Geologic Survey (USGS)
Toxic Substances Hydrology Program
http://toxics.usgs.gov/sites/upper_ark_page.html

The USGS has a few projects in Colorado and elsewhere that attempt to characterize metal transport in streams affected by mining. Work in the Upper Arkansas Toxic-Substance Hydrology Project began in 1986. The approach is to study chemical processes within a hydrologic context, using a two-step approach. First, we have employed in-stream experimentation to provide data about the processes affecting metals. Second, they have used the resulting data sets to develop and apply solute transport models that help quantify rates and processes. See the Web page for more information about this and other projects.

Idaho

U.S. Department of the Interior - Bureau of Land Management
Idaho Abandoned Mine Lands
http://www.id.blm.gov/aml/index.htm

The program stems from a 1982 report that four dozen livestock had been poisoned by ingestion of lead tailings.

Significant effort has been put into Pine Creek, a tributary of the Coeur d'Alene River, in the Silver Belt region of northern Idaho. Between 1996 and 1998 more than 30,000 cubic yards of tailings were removed from the flood plain to prevent the deposition of the material in the river. Much of the cleanup effort was accomplished through funding by the hazardous materials program, Central Haz Mat Fund, and emergency flood funding.

Systematic AML site inventories began in mid-1990s.

Starting in the fiscal year 1999, Clean Water Action Plan funding enabled a more uniform national effort to move from inventory to cleanup of AML sites. Project summaries of completed or active projects can be found in the AML Project Notebook link at http://www.id.blm.gov/aml/notebood.htm

In FY 2002, 2 projects using passive treatment were installed: Champagne Creek and Bridge Creek.

At the beginning of fiscal year 2002, the focus was to better integrate AML with other statewide Idaho priorities. "Lack of a national source of funding dedicated to addressing physical hazards continues to be an issue. This year we are seeking a reallocation of some of Idaho's BLM program funding to better address priority sites, particularly in the proximity of recreation sites and other public lands heavily visited by the public" (http://www.id.blm.gov/aml/program.htm).

Basin Environmental Improvement Project Commission

http://www.basincommission.com/

This organization was created by the Idaho legislature under the Basin Environmental Improvement Act of 2001; the group became operation in March of 2002. It consists of representatives of the state of Idaho, the three Idaho counties in the Basin, the Coeur d'Alene Tribe, the state of Washington, and the United States of America (represented by the U.S. EPA). It is the policy of the state to provide a system for environmental remediation, natural resource restoration and related measures to address heavy metal contamination in the Coeur d'Alene Basin.

Montana / Dakotas

Department of Environmental Quality

Mine Waste Cleanup Bureau

http://www.deq.state.mt.us/rem/mwc/index.asp

The Mine Waste Cleanup Bureau (MWCB) focuses on two primary site types:

1) inactive mine sites addressed under the Surface Mining Coal and Reclamation Act (SMCRA 1977).

2) mining related sites addressed under the Federal Comprehensive Environmental Response and Liability Act (CERCLA) .

The MWCB divided its site-reclamation duties in this way because of distinctions between applicable environmental laws and associated funding mechanisms.

The DEQ-MWCB must give priority to abandoned coal mines, and Montana has completed reclamation of its abandoned coal mines and has now moved on to non-coal sites. The non-coal sites are ranked in priority order based on a scoring system developed by the state. To date, Montana's abandoned mine reclamation program has overseen the completion of more than 283 projects totaling nearly 1174 acres.

U.S. Department of the Interior - Bureau of Land Management

Montana/Dakotas Abandoned Mine Land Program

http://www.mt.blm.gov/aml/index.html

Montana BLM has been working to clean up abandoned mines located on public lands utilizing a watershed approach since 1995. An inventory of 1078 abandoned mines located on public lands resulted in 65 sites that needed further investigation and potentially reclamation.

At least 15 projects are underway or completed. More information can be obtained from the Web page cited above.

Navajo Nation

Division of Natural Resources

Navajo AML Reclamation/UMTRA [Uranium Mill Tailings Radiation Control Act] Department

http://www.navajoaml.osmre.gov

This program was certified to have reclaimed all Priority 1 and 2 abandoned coal mines by the Secretary of Interior as of May 4, 1994 . The program is now permitted to focus attention on non-coal mines. The Navajo AML Program anticipates having all known and eligible abandoned mines reclaimed by the end of 2004.

In 2000, the Navajo AML Program amended its AML Plan to incorporate the provisions of SMCRA, Sections 411(e) and (f), which provide the authority for using AML funds to construct public facilities as a means of mitigating current and past mining-related impacts to such communities. Thus, the Navajo AML Program can now also use its AML funds for the construction of Public Facility Projects (PFP's). Navajo AML funded its first PFP in EY-2002.

In 2002, four reclamation projects were completed, all of the work done "minimized the need for maintenance, promotes landscape stability, enhances re-establishment of natural vegetation, enhances wildlife, and most importantly, adequately safeguards the physical and radioactive hazards."

> - Office of Surface Mining Reclamation and Enforcement : Annual Evaluation Report - Evaluation Year 2002 (Oct. 1, 2001 through Sept. 30, 2002) - on the Navajo Abandoned Mine Lands Reclamation Program.
> http://www.navajoaml.osmre.gov/News_Rprts/AML/OSM_AER_Nav2002.pdf

Nevada

State of Nevada Commission on Mineral Resources
Division of Minerals
400 W. King Street, Suite 106
Carson City, Nevada 89703
(775) 684-7040
fax: (775) 684- 7052
http://minerals.state.nv.us/

The state's first priority is to reduce hazards such as high walls, embankments, etcetera. It is estimated that the state has 200,000 abandoned mine features. Approximately 50,000 present physical safety hazards, including 9,244 hazardous mine openings throughout the state. Seven thousand have been secured.

As for environmental problems, the State of Nevada has an Interagency Abandoned Mine Land Environmental Task Force. In their Sept. 1999 report, an estimated 1 to 3 percent of 200,000 to 500,000 abandoned mine land features have the potential to impact ground or surface waters. Even at 1 percent the numbers are very high--20,000 to 60,000 potential pollution sources. As of 1999 there were 33 sites identified for clean-up; 6 of these sites were considered high priority and site characterization had begun. The report can be reviewed at: http://minerals.state.nv.us/forms/aml/nvamlreport.pdf

U.S. Department of the Interior - Bureau of Land Management
Nevada
http://www.nv.blm.gov/AML/

In March of 1999, the Bureau of Land Management-Nevada State Office (BLM) initiated the formation of an Interagency Abandoned Mine Land Environmental Task Force (IAMLET) to begin remediation of abandoned mine land (AML) environmental problems associated with watersheds in Nevada. The task force is comprised of federal and state agencies with a role in abandoned mine lands in the state. Initial funding for the program is from the BLM through the Soil, Water, and Air Management Budget, in accordance with the Clean Water Action Plan.

> - From the report, 1999 Interagency Mined Land Environmental Task Force Report, found on the webpage above.

Their accomplishments as of March 1999 included:

- Initiation of cleanup of two AML sites (Steward and Atronics millsites) in priority watershed;
- Establishment of site selection criteria for potential AML reclamation projects;

- Compilation of an initial list of 33 AML sites based on proximity and potential impacts to watersheds and assignment of a priority rank to each site;

- Initiation of data compilation, including location and land status maps, existing site characterizations, and photographs for the 33 sites.

The groups involved with this Interagency are:

Bureau of Land Management, BLM

United States Forest Service, USFS

United States Fish and Wildlife Service, USFWS

United States Geological Survey, USGS

Environmental Protection Agency, EPA

Nevada Division of Minerals, NDOM

Nevada Division of Environmental Protection, NDEP

Nevada Division of Wildlife, NDOW

Nevada Bureau of Mines and Geology, NBMG

Desert Research Institute, DRI

New Mexico

New Mexico Energy, Minerals and Natural Resources Department

Mining and Minerals Division

Abandoned Mine Land Program

http://www.emnrd.state.nm.us/Mining/aml/default.htm

The program was formed when SMCRA was passed in 1977. The description of this program states: “the fund is used to reclaim coal mines abandoned prior to the enactment of SMCRA. Under certain conditions, abandoned noncoal mines may also be reclaimed.” The most common mine hazards in NM are open adits and shafts. There are other concerns, including burning gob piles and acid mine drainage.

New Mexico Energy, Minerals and Natural Resources Department

Mining and Minerals Division

Mining Act Reclamation Program

http://www.emnrd.state.nm.us/Mining/marp/default.htm

This program was created under the New Mexico Mining Act of 1993 to regulate hard rock mining reclamation activities for all minerals except potash, sand, gravel, quarry rock used as aggregate in construction, flagstone, calcite, clay, adobe, borrow dirt, activities regulated by the Nuclear Regulatory Commission, and waste regulated under Subtitle C of the Federal Resource Conservation and Recovery Act.

New Mexico Energy, Minerals and Natural Resources Department

Ground Water Quality Bureau

Mining Environmental Compliance Section

Active mines are handled through this office when water quality is an issue. Upon speaking with Mark Phillip of this office, it became clear that most of their work involves water diversion and water treatment plants.

Wyoming

Department of Environmental Quality (DEQ)

Abandoned Mine Land

http://deq.state.wy.us/aml

AML's mission is to eliminate safety hazards and repair environmental damage from past mining activities and to assist communities impacted by mining. AML pursues this mission in two ways:

1. The Traditional Reclamation Program which has reclaimed thousands of acres of abandoned coal, bentonite, and uranium open pit mines, and new projects are initiated each year. AML has also closed several hundred hazardous gold and copper mine openings, and has an ongoing program to mitigate subsidence risks. AML also makes subsidence insurance available to property owners in affected communities.
2. The Public Facility Program, operating in conjunction with the State Loan and Investment Board, provides financial assistance for projects in communities with current or past impact from mining. Applicants must first establish eligibility, then projects are ranked and funded based on human health and safety issues.

U.S. Department of the Interior - Bureau of Land Management

Abandoned Mine Land Reclamation

http://www.wy.blm.gov/whatwedo/aml/aml_home.html

Wyoming BLM works closely with DEQ to share resources and pool funding. The projects listed on the Web page did not use any innovative treatments.

Inventory of the sites and the work needed at each was expected to be done by the end of 2001.

Appendix B: Brief Case Description of Case Studies Found in This Report

Site	Location	Mine Information	Pollution (media)	Treatment	Page
North Pennine Orefield	Nent Valley, UK	Metal/Hardrock	Zn (water)	Anoxic Limestone Drain	12
Burleigh Tunnel	Silver Plume, CO	Metal/Hardrock	Zn (water)	Constructed Wetland	14
Calliope Mine	Silver Bow, MT	Metal/Hardrock	Al, As, Cd, Cu, Fe, Mn, Zn, low pH (water)	Bioreactor	15
Champagne Creek	Butte, ID	Metal/Hardrock	Al, Cd, Cu, Fe, Zn, low pH (water)	Bioreactor	16
Oven Run	Pennsylvania	Coal	Fe, Al, low pH (water)	Successive Alkalinity Producing System	18
Gowen Run	Gowen, OK	Coal	Fe, other metals, low pH (water)	Successive Alkalinity Producing System	18
	Frostburg, MD	Coal - strip mine	metals, low pH (soil)	Biosolids	21
	Leadville, CO	Metal/Hardrock	Zn, Pb, low pH (soil)	Biosolids	23

Exhibit M:

The Passive Treatment of Coal Mine Drainage

DOE/NETL-2004/1202

The Passive Treatment of Coal Mine Drainage

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Abstract

Passive treatment of mine water uses chemical and biological processes to decrease metal concentrations and neutralize acidity. Compared to conventional chemical treatment, passive methods generally require more land area, but use less costly reagents, and require less operational attention and maintenance. Currently, the three most common types of passive technologies are aerobic ponds and wetlands, anoxic limestone drains (ALDs), and reducing and alkalinity-producing systems (RAPS). Aerobic wetlands promote mixed oxidation and hydrolysis reactions, and are effective when the raw mine water is net alkaline. Anoxic limestone drains generate bicarbonate alkalinity and can be used to convert water that is net acidic into net-alkaline water for treatment in aerobic ponds and wetlands. RAPS promote reducing conditions and limestone dissolution. They extend the concept of ALDs by pre-treating the water before it contacts the limestone, to eliminate dissolved oxygen and reduce dissolved ferric iron to ferrous iron. These systems can generally be used to treat more acidic water than ALDs, and can better treat water with significant aluminum concentrations.

In passive treatment systems, rates of metal and acidity removal and alkalinity generation have been developed empirically. Aerobic wetlands remove iron from alkaline water at rates of 10 to 20 g $m^{-2}\,d^{-1}$. Anoxic limestone drains add 150 to 300 mg/L of alkalinity in about 15 hours of contact, imparting 5 to 20 mg/L of alkalinity per hour of contact. Reducing and alkalinity-producing systems add 15 to 60 g $m^{-2}\,d^{-1}$ of alkalinity, depending on influent water quality and contact time. Selection and sizing criteria for the design of passive treatment systems are presented in this report.

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Contents

Figures

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Introduction

Treatment of Mine Water

In the United States, mining companies commonly treat contaminated drainage using conventional chemical methods. In most conventional treatment systems, metal contaminants are removed through the constantly measured addition of alkaline chemicals (e.g., NaOH, $Ca(OH)_2$, CaO, Na_2CO_3, or NH_3) to meet Federal effluent limits. (See Table 1.) These are maximum concentrations allowed for active coal mining operations. Some operators have much more stringent effluent limits, based on the quality of the receiving stream. The chemicals used in these treatment systems can be expensive, especially when required in large quantities. In addition, there are operation and maintenance costs associated with aeration and mixing devices, and additional costs associated with the disposal of the metal-laden sludge that accumulates in settling ponds. It is not unusual for water treatment costs to exceed $10,000 per year at sites that are otherwise successfully reclaimed. The high cost of water treatment places a serious financial burden on active mining companies, and has contributed to the bankruptcy of many others.

The high cost of conventional chemical systems limit water treatment efforts at abandoned sites. Thousands of miles of streams and rivers in Appalachia are currently polluted by drainage from sites that were mined and abandoned before enactment of effluent regulations. State and Federal reclamation agencies, local conservation organizations, and watershed associations all consider the treatment of contaminated mine discharge to be a high priority. However, insufficient funds are available for chemical water treatment, except in a few watersheds of special value.

Table 1. Federal Effluent Limits for Coal Mine Drainage

Parameter	**Maximum for Any One Day**	**Average of Daily Values for 30 Consecutive Days**
Iron, total (mg/L)	6.0	3.0
Manganese, total (mg/L)	4.0	2.0
Total suspended solids (mg/L)	70	35
pH (standard units)	between 6.0 and 9.0	

During the past 20 years, the possibility that mine water might be treated passively has developed from an experimental concept to full-scale field implementation at hundreds of sites throughout the world (Younger et al. 2002, Brown et al. 2002). Passive technologies take advantage of the natural chemical and biological processes that ameliorate contaminated water conditions. Ideally, passive treatment systems require no constant input of chemicals, and little maintenance. Passive treatment systems use contaminant removal processes that are slower than conventional treatment and thus require longer retention times and larger areas to achieve similar results. The goal of the passive mine drainage treatment system is to enhance natural ameliorative processes, so that they occur within the treatment system, not in the receiving water body. Two factors that determine whether this goal can be accomplished are the kinetics of the contaminant removal processes, and the retention time of the mine water in the treatment system. The retention time for a particular mine site is often limited by available land area. However, the kinetics of contaminant removal processes can often be affected by manipulating the environmental conditions that exist within the passive treatment system. Efficient manipulation of contaminant removal processes requires an understanding of of each removal process and their respective limitations..

History of Passive Treatment

Passive treatment of mine water can be traced to two independent research projects which showed that natural wetlands were ameliorating mine drainage without incurring any obvious ecological damage. Researchers at Wright State University studied a site in the Powelson Wildlife Area in Ohio where *Sphagnum recurvem* had volunteered and was growing in pH 2.5 water. As the water flowed through the boggy area, iron, magnesium, calcium, sulfate, and manganese all decreased, while pH increased to 4.6. A natural outcrop of limestone located at the downstream end provided sufficient neutralization to raise the effluent pH to between 6 and 7 (Huntsman et al. 1978). Meanwhile, a similar study was being conducted by a group at West Virginia University, working at a natural *Sphagnum*-dominated wetland, Tub Run Bog, in northern West Virginia. They were looking at the ecological damage to the wetland as a result of drainage water from an adjoining abandoned mine. They found no adverse ecological effects, and that in fact, within 20 to 50 m of the influent, the pH of the water rose from between 3.05 and 3.55 to 5.45 and 6.05. Sulfate concentrations decreased to 15 mg/L or less, and iron decreased to less than 2 mg/L (Wieder and Lang 1982). These field observations prompted the idea that wetlands might be constructed for the intentional treatment of coal mine drainage. It was thought that the small seeps present at many abandoned mine sites could be passively treated in this manner. Research efforts were initiated by the United States Bureau of Mines, in cooperation with Wright State University (Kleinmann et al. 1983, Kleinmann 1985). Independently, West Virginia University, and subsequently, Pennsylvania State University conducted research as well (e.g., Gerber et al. 1985, Stone and Pesavento 1985).

Initially, most of these experimental wetlands were constructed to mimic the *Sphagnum* wetlands. However, *Sphagnum* moss was not readily available, proved difficult to transplant, and tended to accumulate metals to levels that were toxic to the *Sphagnum* after several months of exposure to mine drainage (Huntsman et al. 1985, Spratt and Wieder 1989). Instead of abandoning the concept, researchers experimented with different kinds of constructed wetlands. Eventually a wetland design evolved that proved tolerant to years of exposure to contaminated mine drainage and was effective at lowering concentrations of dissolved metals. Most of these treatment systems consisted of a series of small wetlands (< 1 ha) that were vegetated with cattails (*Typha latifolia*) (Girts et al. 1987, Stark et al. 1990). Although neither were as acid tolerant or as effective in removing metals as the *Sphagnum* systems, the cattail systems proved to be very hardy. We gradually learned that these systems were very cost effective in treating circumneutral and net alkaline mine water, where the primary objective was to precipitate the iron in the wetland, instead of downstream.

Some of these wetlands were constructed with a compost and limestone substrate to provide a favorable environment for the cattails to root. Others were constructed without an exogenous organic substrate; emergent plants were rooted in whatever soil or spoil substrate was available on the site when the treatment system was constructed. Researchers soon realized that the cattails were generally collecting only a small component of accumulated metals internally (Sencindiver and Bhumbla 1988), and that its principal functions were dispersing the flow of the water and filtering out the suspended floc of the precipitated metals (some recent research indicates that plant uptake of iron at low concentrations may be critical to achieving very low residual iron concentrations (Batty and Younger 2002)). Subsequently, some systems were constructed that did not rely at all on the early wetland model . Ponds, ditches, and rock-filled basins were constructed without emergent plants and, in some cases, without soil or organic substrate.

In the late 1980s, two new approaches were developed that extended the treatment capabilities of wetlands to more acidic mine water. In the first case, U. S. Bureau of Mines researchers, assessing the performance of a wetland that had been constructed in an attempt to treat very acidic water, found that in isolated locations, the mine water was being neutralized and iron was being precipitated as a sulfide. Apparently, water was flowing down through the compost/limestone substrate and then back up again, gaining alkalinity in the process (Hedin et al. 1988). An approach was developed to optimize this effect and was evaluated in the field (McIntyre and Edenborn 1990, Nawrot 1990), these anaerobic or compost wetlands added alkalinity, but were not very efficient for iron removal, and required sequential placement of aerobic and anaerobic systems. Currently, these systems are seldom constructed to treat coal mine drainage, however, they can be useful for treatment of metal mine drainage, since they provide a mechanism to remove metals such as cadmium, copper, lead, etc. (Wildeman et al. 1990, Wildeman et al. 1994).

The other new approach involved acidic water in contact with limestone in an anoxic environment before flowing into a settling pond or wetland system. Although limestone had previously been used many times to treat mine water, it typically became coated or “armored” by iron hydroxide. Turner and McCoy (1990) reasoned that if the mine water could be intercepted before it contacted the atmosphere, and was directed into a limestone-filled French drain, the dissolved iron would not oxidize to ferric hydroxide to armor the limestone, and the water would be neutralized. The water could then be discharged into an aeration pond and a wetland. A great number of anoxic limestone drains (ALDs) were subsequently constructed, and soon, sizing guidelines were developed (Hedin et al. 1994b). However, as discussed in more detail later in this manual, these systems also had their limitations. They worked well for mildly acidic water ($pH > 4.5$) that was anoxic, but more acidic water tended to contain dissolved aluminum, which precipitated in the ALD and reduced permeability, often to the point of failure. In addition, if the pH of the water was below about 3.5, the dissolved iron was often already oxidized (ferric), so that armoring could occur even if no oxygen was present.

To compensate for dissolved oxygen and dissolved ferric iron, the concept of the ALD and compost wetland were combined (Kepler and McCleary 1994, Kepler 1995). Compost was placed up-gradient of the limestone. The bacterial activity in the compost consumed the dissolved oxygen and reduced the ferric iron to ferrous iron, allowing the ALD component to work as intended, even for very acidic water. They referred to these systems as sequential alkalinity-producing systems (SAPS); others have preferred to use the term reducing and alkalinity producing systems (RAPS) to more accurately describe the process, and to include systems that did not put more than one unit in sequence. These systems are also called vertical flow ponds, vertical flow wetlands or vertical flow systems. Aluminum is still retained in these systems, so Kepler and McCleary (1997) suggested a simple gravity-powered flushing mechanism to extend their effective life span.

It is difficult to argue with the long-term success of some of these passive treatment systems. However, failures can be very damaging to the perceived effectiveness of the technology. In general, we have found that the systems that were not effective or failed were undersized, improperly designed, or both. The key is to understand the limitations of each unit's operation, to have reasonable expectations, and to use conservative sizing criteria to attain specific water quality goals. Even undersized passive systems can be useful, discharging water with significantly lower concentrations of metal contaminants than present in the inflow drainage. These improvements in water quality decrease the costs of subsequent water treatment at active sites, and decrease deleterious impacts that discharges from abandoned sites have on receiving streams and lakes.

Researchers have recently developed additional passive treatment technologies, such as steel slag leach beds (Simmons et al. 2002), which may prove to be useful additions to the passive treatment arsenal. Research is being conducted on semi-passive approaches that have the potential to significantly reduce the land requirements of passive treatment systems. Semi-passive systems fall between conventional chemical treatment, which requires virtually around-the-clock attention, and passive systems that ideally require very little maintenance and attention (Younger et al. 2002). Semi-passive systems have been constructed using gravity-, wind-, and water-powered aeration or neutralization processes, as well as some low-power demanding devices.

Background

Formation of Polluted Mine Waters

The cause of most mine water degradation is the oxidation of iron sulfide minerals, such as pyrite (FeS_2). Equal amounts of acidity are produced by the oxidation of the sulfide to sulfate (reaction A), and by the oxidation and hydrolysis of iron (reaction B) (Barnes and Romberger 1968):

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad \text{(A)}$$

$$Fe^{2+} + 2.5H_2O + 0.25O_2 \rightarrow Fe(OH)3(s) + 2H^+ \qquad \text{(B)}$$

Iron-oxidizing bacteria accelerate pyrite oxidation by two mechanisms: direct oxidation, and oxidizing Fe^{2+} to Fe^{3+}, which in turn oxidizes the sulfide minerals (Beck and Brown, 1968, Duncan et al. 1967, Groudev 1979, Silverman 1967). Direct oxidation is probably most important during initial acidification, when complete hydrolysis of Fe^{3+} and the resultant precipitation of $Fe(OH)_3$ are too rapid to allow ferric iron to act as an important oxidant.

As the pH decreases, abiotic oxidation of Fe^{2+} slows down dramatically, according to the rate law:

$$\frac{-d\,(Fe^{2+})}{dt} = k\,\frac{(O_2\,(aq))\,(Fe^{2+})}{(H^+)^2} \qquad (C)$$

where (Fe^{2+}), $(O_2\,(aq))$, and (H^+) are activities, k is the rate constant, and t is time (Stumm and Morgan 1981). Below approximately pH 4 (Kirby et al. 1999), the iron-oxidizing bacteria assume the primary role of oxidizing Fe^{2+}, thereby allowing reaction B to continue producing acidity and ferric hydroxide. Although the reaction stoichiometry remains the same, this is a transition point from the primarily abiotic stage to the partially biological stage (Kleinmann et al. 1981). The pH decline typically continues to a stage where the reaction chemistry changes to a biologically-mediated cycle of reactions D and E (Kleinmann et al. 1981, Temple and Delchamps 1953):

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow 0.5Fe^{3+} + 0.5H_2O \qquad (D)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (E)$$

As acidification proceeds and the pH in the immediate vicinity of the pyrite falls to less than 3, the increased solubility of iron, and the decreased rate of $Fe(OH)_3$ precipitation result in increased Fe^{3+} activity (Silverman,1967). This is significant because as Fe^{3+} aggressively attacks pyrite, it is reduced to Fe^{2+} (reaction E) for subsequent reoxidation by iron oxidizing bacteria, such as *Acidithiobacillus ferrooxidans* (formerly called *Thiobacillus ferrooxidans*). Oxidation of pyrite by Fe^{3+} is about an order of magnitude faster than oxidation by equivalent concentrations of dissolved oxygen, apparently because of different reaction mechanisms at the molecular level (Luther 1987). When the pH in the immediate microenvironment of the pyrite falls to approximately 2.5 (often corresponding to a drainage pH of 3.5 to 4.0), bacterial oxidation of Fe^{2+} and reduction of Fe^{3+} by the pyrite (reactions D and E) combine to cause a dramatic increase in acidity and iron concentrations (Kleinmann 1979).

As this solution moves through mine workings or spoils, it undergoes secondary reactions that raise pH, decrease concentrations of iron, and increase the concentrations of other cations. Contact with clays and other aluminosilicates releases aluminum, sodium, potassium, and magnesium, while contact with carbonate minerals releases calcium, magnesium, manganese, and additional iron (siderite). The various effects these reactions have on the chemistry of the mine drainage depends on the volume of water, the amount of pyrite oxidized, and the extent and variety of secondary chemical reactions. The secondary reactions can produce a drainage with relatively high sulfate concentrations, butcircumneutral pH (Kleinmann et al. 1983, Stone and Pesavento 1985), is low in metals, and fairly innocuous. Alternatively, the mine water may have circumneutral pH, but contains elevated concentrations of dissolved iron and manganese, and can become acidic (pH ~3) upon oxidation and precipitation of iron. In other cases, the mine drainage is acidic; acid mine drainage often contains high concentrations of dissolved iron, aluminum, and manganese. Both alkaline and acidic mine drainage may contain other metals, namely zinc, nickel, and cobalt.

As contaminated mine drainage flows through receiving systems (streams, rivers, and lakes), its toxic characteristics decrease naturally as a result of chemical and biological reactions, and dilution with uncontaminated waters. Under the aerobic conditions found in most surface waters, iron, aluminum, and manganese precipitate as oxides and hydroxides. Ferrous iron oxidizes to ferric iron, which hydrolyzes and precipitates mainly as iron oxyhydroxides (e.g., FeOOH) or oxyhydroxylsulfates of various composition and crystallinity. These compounds stain the bottom of many streams orange, often accumulating at sufficient depths to suffocate benthic organisms. The rate of iron precipitation at low pH depends on the activity of the same iron-oxidizing bacteria that catalyze pyrite oxidation (e.g., *A. ferrooxidans*); the abiotic rate increases a hundredfold for every unit increase in pH, and is also dependent on the amount of oxygen dissolved in the water. (See reaction C.)

Aluminum generally hydrolyzes and precipitates as $Al(OH)_3$, which is a white particulate. Other aluminum compounds with silica and sulfate can also form, depending on the environmental conditions. Oxidation is not required, and apparently bacterial activity is not a factor. Precipitation of aluminum requires a pH above 4, and is generally observed at a pH of 4.5 or above. Aluminum solids will become soluble, as $Al(OH)_4^-$, and at pH levels over 8.5. This can occur in conventional chemical treatment systems that must increase pH to these higher levels to remove manganese.

Manganese oxidizes and hydrolyzes to MnOOH or MnO_2, and precipitates as a black particulate. Ubiquitous manganese-oxidizing bacteria can influence the rate of removal, since like iron, oxidation generally precedes precipitation. More important however, is that significant oxidation and precipitation of manganese requires a pH greater than 6, and generally only occurs in passive systems after virtually all of the iron has already precipitated. As a result, manganese removal, if necessary, significantly increases the land area required for passive treatment. Manganese precipitation is auto-catalytic; once precipitates form, their presence increases the rate of manganese removal. In conventional chemical treatment systems, the pH is often raised above 9 or 10 to remove manganese to desired levels.

Chemical Characteristics of Mine Drainage

Acidity

Acidity is a measurement of the base neutralization capacity of a volume of water. Four types of acidity exist: organic acidity associated with dissolved organic compounds, carbon dioxide acidity associated with dissolved carbon dioxide and carbonic acid; proton acidity associated with pH (a measure of free H^+ ions); and mineral acidity associated with dissolved metals (Hem 1985). Mine waters generally have very little dissolved organic carbon, so organic acidity is very low. The amount of dissolved carbon dioxide in mine drainage varies with geologic and environmental conditions and usually only contributes significantly to acidity at pH levels > 5. In addition, carbon dioxide acidity can be thought of as temporary, because CO_2-rich waters will degas upon exposure to the atmosphere. The majority of acidity in coal mine drainage arises from free protons (manifested in low pH) and the mineral acidity arising from dissolved iron, aluminum, and manganese. These metals are considered acidic because they can undergo hydrolysis reactions that produce H^+.

$$Fe^{2+} + 0.25O_2 + 1.5H_2O \rightarrow FeOOH + 2H^+ \qquad (F)$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+ \qquad (G)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (H)$$

$$Mn^{2+} + 0.25O_2 + 1.5H_2O \rightarrow MnOOH + 2H^+ \qquad \text{(I)}$$

These reactions can be used to calculate an estimate of the total acidity of a mine water sample, and to partition the acidity into its various components. The expected acidity of a mine water sample is calculated from its pH and the sum of the milliequivalents of the dissolved acidic metals. For most coal mine drainages, the acidity is calculated as follows,

$$Acid_{calc} = 50(2Fe^{2+}/56 + 3Fe^{3+}/56 + 3Al/27 + 2Mn/55 + 1000(10^{-pH})) \qquad (1)$$

where all metal concentrations are in mg/L, and 50 is the equivalent weight of $CaCO_3$, and thus transforming mg/L of acidity into mg/L as $CaCO_3$ equivalent. Simplifying the equation shows the conversion factors to be applied to each dissolved metal and hydrogen ion concentration (pH):

$$Acid_{calc} = 1.79Fe^{2+} + 2.68Fe^{3+} + 5.56Al + 1.82Mn + 50{,}000(10^{-pH}) \qquad (2)$$

Equation 2 accurately characterizes mineral and proton acidity for most samples of actual acid mine drainage. It must be emphasized that only dissolved metals add to acidity, not those already precipitated. Figure 1 shows a very good correlation ($R^2 = 0.9943$ and slope = 1.026) between measured and calculated acidity for mine drainage samples collected at over 150 different sites.

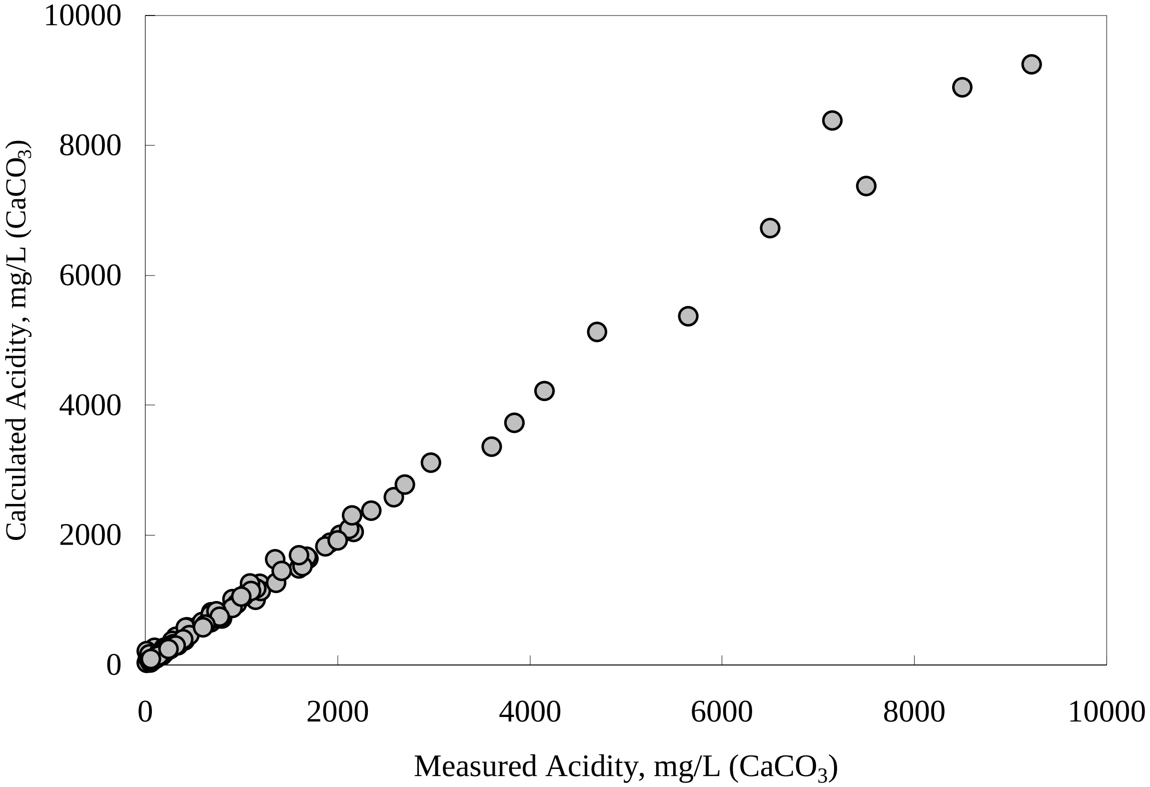

Figure 1. Calculated Versus Measured Acidity for Over 150 Coal Mine Discharges

Equation 2 can be used to partition total acidity into its individual constituents. When the total acidity of contaminated coal mine drainages is partitioned in this manner, the importance of mineral acidity becomes apparent. Table 2 shows a breakdown of the acidic components of three mine drainages. At each site, the acidity arising from protons (pH) was never the largest contributor to total acidity. Only when pH is less than 3.5 does it contribute significantly to acidity. (See Table 3.)

Table 2. Contributions of Metal Concentration and pH to Acidity for Selected Mine Discharges

	Howe Bridge			Jennings			Oven Run E			Elklick		
	Value	**A.C.**	**%**	**Value**	**A.C.**	**%**	**Value**	**A.C.**	**%**	**Value**	**A.C.**	**%**
pH	5.38	<1	<1	3.35	22	6	2.74	91	34	5.79	<1	<1
Fe^{2+}	225	402	88	60	107	31	<1	<1	<1	55	98	93
Fe^{3+}	<1	<1	<1	4	11	3	20	54	20	<1	<1	<1
Al^{3+}	<1	<1	<1	30	167	48	18	100	37	<1	<1	<1
Mn^{2+}	29	53	12	22	40	12	13	24	9	4	7	7

pH in standard units. Fe^{2+}, Fe^{3+}, Al^{3+} and Mn^{2+} concentrations in mg/L. A.C. is acidity contribution in mg/L as $CaCO_3$.

Table 3. Proton Acidity Contributions at Various pH Values

pH	**Acidity Equivalent (mg/L as $CaCO_3$)**
6.0	0.05
5.0	0.5
4.5	1.6
4.0	5
3.5	16
3.0	50
2.5	158
2.0	500

Alkalinity

When mine water pH is greater than 4.5, it has acid neutralizing capacity and is said to contain alkalinity. Alkalinity can result from hydroxyl ion (OH^-), carbonate, silicate, borate, organic ligands, phosphate, and ammonia (Hem 1985). The principal source of alkalinity in mine water is dissolved carbonate, which can exist in bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}) form. Both can neutralize proton acidity (reactions J and K). In the pH range of most alkaline mine waters, bicarbonate is the principal source of alkalinity (Wieder and Lang 1982, Stone and Pesavento 1985).

$$2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2 \qquad (J)$$

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \qquad (K)$$

The presence of bicarbonate alkalinity in mine waters with elevated levels of metals is not unusual, particularly in anoxic waters. Table 4 shows the chemical composition of six mine waters in northern Appalachia that contain alkalinity, and are also contaminated with ferrous iron and manganese. None are contaminated with significant levels of dissolved ferric iron or aluminum because the solubilities of these metal hydroxides are low in mine waters with pH greater than 5.0 (Hem 1985, Stumm and Morgan 1981).

Table 4. Chemical Composition of Untreated Mine Waters Containing Alkalinity

	pH	Alkalinity	Fe^{2+}	Fe^{3+}	Al^{3+}	Mn^{2+}	Net Acidity	Calculated Acidity
Penn Allegh	6.64	470	76	<1	<1	2	-358	-330
Brinkerton	6.04	168	50	<1	<1	1	-101	-77
Scrubgrass	6.00	165	64	<1	<1	<1	-61	-50
Elklick	5.79	42	54	<1	<1	4	62	62
Howe Bridge	5.38	35	225	<1	<1	37	395	435
Morrison	5.15	23	229	<1	<1	47	373	472

Alkalinity and pH were determined in the field. Metals and net acidity were analyzed in the lab. Calculated acidity was calculated using Equation 2 subtracting field alkalinity. pH in standard units, alkalinity and acidity in mg/L as $CaCO_3$, metal concentrations in mg/L. Negative values of acidity indicate net alkalinity.

Alkalinity and acidity are not mutually exclusive terms. All of the mine waters shown in Table 4 contain both acidity and alkalinity. When water contains both mineral acidity and alkalinity, a comparison of the two measurements results in a determination as to whether the water is net alkaline (alkalinity > acidity) or net acidic (acidity > alkalinity). Net alkaline water contains enough alkalinity to neutralize the mineral acidity represented by dissolved ferrous iron and manganese. As these metals oxidize and hydrolyze, the produced proton acidity is rapidly neutralized by bicarbonate. For waters contaminated with Fe^{2+}, the net reaction for the oxidation, hydrolysis and neutralization reactions is:

$$Fe^{2+} + 0.25O_2 + 2HCO_3^- \rightarrow FeOOH + 0.5H_2O + 2CO_2 \qquad (L)$$

Reaction L indicates that net alkaline waters contain at least 1.8 mg/L alkalinity for each 1.0 mg/L of dissolved Fe^{2+}. Waters that contain a lesser ratio are net acidic; the oxidation and hydrolysis of the total dissolved iron content results in a net release of protons and a decrease in the pH. For waters containing dissolved Fe^{2+}, accurate determination of alkalinity must be performed in the field, immediately upon the collection of water samples. Laboratory determinations may lead to incorrect conclusions, due to reaction L occurring in the sample bottle, thus decreasing measurable alkalinity concentrations.

Interpretation of Laboratory Analyses

There has been, and continues to be some confusion interpreting the results of net alkaline or net acidic laboratory analyses (Kirby 2002). Selection of the most effective passive treatment system design depends on whether the water is net acidic or net alkaline. Interpretation confusion arises from the way laboratories report the acidity and alkalinity values. They report acidity and alkalinity in mg/L as $CaCO_3$. The analytical procedure in *Standard Methods* (APHA 1998), however, actually measures net acidity for the acidity method, and gross alkalinity for the alkalinity method, and offers no guidance for reporting acidity and alkalinity as a net or gross value, respectively. The 20th edition of *Standard Methods* instructs the lab to report "the acidity to pH ___ = ___ mg as $CaCO_3$/L" and "the alkalinity to pH ___ = ___ mg as $CaCO_3$/L." The wording was even less clear in previous editions (APHA 16th edition 1985), which stated "if a negative value is obtained, determine the alkalinity according to [the chapter on alkalinity]." It does not instruct the lab what to do with this negative number. Many labs reported that acidity was zero or left a blank space for the acidity value. Some labs list the acidity value as negative. The labs performed the alkalinity titration and recorded the value obtained as alkalinity. The problem lies with the individual interpretation of these results. For example, the table below shows two different water qualities:

Water	**pH**	**Potential Acidity as Fe^{2+} and/or Mn^{2+} (mg/L as $CaCO_3$)**	**Alkalinity (mg/L as $CaCO_3$)**	**True Net Acidity* (mg/L as $CaCO_3$)**
A	6.2	100	105	-5
B	6.1	150	100	50

* *Negative numbers denote net alkalinity.*

If a laboratory analyzed this water and if they received a negative number for acidity (for water A), they reported it as zero, and their lab sheet would look like this:

Water	**pH**	**Acidity (mg/L as $CaCO_3$)**	**Alkalinity (mg/L as $CaCO_3$)**
A	6.2	0	105
B	6.1	50	100

For water A, most labs would interpret the results as having a net alkalinity of 105 mg/L (as $CaCO_3$), when, in fact, the water is only barely net alkaline (5 mg/L). If the lab reported acidity simply as negative, there was still confusion about whether the water was net alkaline or net acidic. Most would interpret water B, which is truly net acidic (50 mg/L as $CaCO_3$), as being net alkaline (50 mg/L as $CaCO_3$).

For water B, the important concept to remember is that the value obtained in the acidity titration is a *net value*. Since the lab reported acidity as 50 mg/L, this indicates that the water is net acidic (of 50 mg/L). For water A, if the laboratory reported the negative number that they actually received for acidity, it would eliminate the confusion. In 1998, authors of *Standard Methods* recognized this fact, and clarified their instruction in the 20th edition, instructing the reader: "if a negative value is obtained, report the value as negative. The absolute value of this negative value should be equivalent to the net alkalinity." It is still not clearly stated to report either positive or negative numbers as *net acidity*.

To complicate matters even further, some laboratories realized that if the water contained alkalinity, that this was consumed in the acidity titration and functioned to lower the value obtained in the titration. They then added the alkalinity value to the value obtained in the acidity titration and entered that for the acidity value. In essence they were listing the true gross values for acidity and alkalinity. For water A, they would list acidity as 100 mg/L as$CaCO_3$ and alkalinity as 105 mg/L as $CaCO_3$. For water B, they would list acidity as 150 mg/L and alkalinity as 100 mg/L as $CaCO_3$. The simple subtraction of these two values would result in the correct interpretation, if the laboratory realized that gross values were being reported. If the laboratory knew that the value for acidity in *Standards Methods* was typically a net value, they would believe that both water samples were net acidic.

To ensure the correct interpretation of the values that laboratories provide, the laboratory must be contacted to determine what values they reported. Laboratories should report the value of any negative numbers they obtain in the acidity titration. If they follow the procedures outlined in *Standard Methods*, the value for acidity is the *net value* with negative numbers indicating *net* alkalinity, and the alkalinity value is the *gross* alkalinity.

As stated earlier, to ensure accurate measurement of alkalinity, the analysis should be performed in the field. If ferrous iron is in the sample, oxidation and subsequent hydrolysis can significantly lower alkalinity concentrations.

Concentrations of other constituents in coal mine drainage vary, depending on geologic and environmental conditions. Table 5 lists the mean, median, and ranges of several chemical parameters associated with 156 different coal mine drainage discharges.

Table 5. Water Quality from 156 Coal Mine Discharges

Parameter	Times Reported	Mean	Median	Minimum	Maximum
Flow	54	601	71.5	5.50	15600
pH	156	4.03	3.37	2.18	7.80
Conductivity	64	2500	2000	320	8140
Alk, field	95	32.0	0	0	470
Acidity	151	909	315	-358	9220
Sulfate	156	1750	1220	67.5	1100
Aluminum	156	68.4	15.6	0	930
Antimony	120	0.006	0	0	0.200
Arsenic	142	0.040	0	0	2.95
Barium	135	0.010	0	0	0.200
Beryllium	140	0.017	0	0	0.270
Cadmium	146	0.006	0	0	0.200
Calcium	156	168	159	6.90	483
Chloride	50	64.1	8.15	0	849
Chromium	155	0.063	0	0	7.18
Cobalt	137	0.646	0.240	0	6.00
Copper	155	0.103	0	0	2.49
Iron, Ferric	140	96.7	4.35	0	2420
Iron, Ferrous	137	150	65.0	0	1610
Iron, Total	156	221	71.9	0	2440
Lead	144	0.009	0	0	0.433
Magnesium	156	104	80.0	2.75	638
Manganese	156	20.6	6.76	0	164
Nickel	150	0.962	0.400	0	10.0
Potassium	143	4.05	3.12	0.04	32.0
Selenium	136	0.013	0	0	0.369
Silver	22	0.0005	0	0	0.010
Sodium	156	45.3	8.70	0.33	712
Vanadium	20	0.115	0.050	0	0.660
Zinc	153	2.64	0.700	0	48.0

All concentrations in mg/L, flow in L/min, pH in standard units, acidity and alkalinity in mg/L as $CaCO_3$*, negative acidity indicates net alkalinity.*

Passive Treatment Processes

Limestone Dissolution

A major source of bicarbonate in many anoxic environments is the dissolution of carbonate minerals, such as calcite.

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3- \qquad (M)$$

Carbonate dissolution can result in higher concentrations of bicarbonate in anoxic mine water environments than oxic environments, for two reasons. First, the absence of ferric hydroxide in most anoxic environments limits the formation of FeOOH coatings that may armor carbonate surfaces and inhibit further carbonate dissolution in oxic environments (U.S. EPA 1983). Second, the solubility of carbonate compounds are directly affected by the partial pressure of dissolved CO_2 (Stumm and Morgan 1996, Hem 1985, Butler 1991). Anoxic mine water environments commonly contain high CO_2 partial pressures due to the decomposition of organic matter and the neutralization of proton acidity. Table 6 shows how the partial pressure of carbon dioxide affects the maximum level of potential alkalinity. At atmospheric levels (~0.0003), only about 60 mg/L of alkalinity (as $CaCO_3$) is capable of being dissolved. However, CO_2 levels can be much higher within soil and mine spoil than in the atmosphere, from 0.01 to 0.10. At these CO_2 levels, alkalinity concentrations of 220 to 475 mg/L are possible.

Table 6. Equilibrium Concentrations of Alkalinity at Various P_{CO2} Levels

P_{CO2} (atm)	Alkalinity (mg/L as $CaCO_2$)
0.0003 (~atmospheric)	60
0.01	220
0.05	360
0.10	475
0.20	610
0.50	850
1.00	1085

The observation that limestone dissolution by mine water is enhanced under closed conditions has resulted in the construction of anoxic limestone treatment systems. The first demonstration of this technology was by Turner and McCoy (1990), who showed that when anoxic acidic mine water was directed through a plastic-covered buried bed of limestone, it was discharged in an alkaline condition.

Since Turner and McCoy described their findings in 1990, dozens of additional limestone treatment systems have been constructed (e.g., Brodie et al. 1991, Skousen and Faulkner 1992). These passive mine water pretreatment systems have become known as anoxic limestone drains (ALDs). In an ALD, mine water is made to flow through a bed of limestone gravel that has been buried to limit contact with atmospheric oxygen. The burial containment also traps CO_2 within the treatment system, allowing the development of high CO_2 partial pressures, which in turn allows additional limestone dissolution (Nairn et al. 1992).

Under oxic conditions, limestone dissolution may be enhanced by the active generation of acidity (hydrogen ion) by ferric iron and aluminum hydrolysis. However, this process may not lend itself to sustainable treatment systems, due to problems of armoring and clogging.

Sulfate Reduction

When mine water flows through an anaerobic environment that contains an organic substrate, the water chemistry can be affected by bacterial sulfate reduction. In this process, bacteria oxidize organic compounds using sulfate as the terminal electron acceptor and release hydrogen sulfide and bicarbonate,

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \qquad \text{(N)}$$

where CH_2O is used to represent organic matter. Bacterial sulfate reduction is limited to certain environmental conditions (Postgate 1984). Bacteria requirea the presence of sulfate, suitable concentrations of low-molecular weight carbon compounds, and the absence of oxidizing agents, such as oxygen, Fe^{3+} and Mn^{4+}. These conditions are commonly satisfied in treatment systems that receive coal mine drainage and are constructed with an organic substrate, such as a compost material. High concentrations of sulfate (> 500 mg/L) are characteristic of contaminated coal mine drainage. The oxygen demand of organic substrates causes the development of anoxic conditions and an absence of oxidized forms of iron or manganese. The low molecular-weight compounds that sulfate-reducing bacteria utilize (lactate, acetate) are common end-products of microbial fermentation processes in anoxic environments. These sulfate reducing and fermentative bacteria are more active above pH ~5, however, they can be very active in drainages with lower pH levels, due to the presence of near-neutral pH microenvironments. These microenvironments allow the sulfate reducing bacteria (SRB) to become established, and because they generate alkalinity, these microenvironments become larger.

Metal Removal Processes

Coal mining can promote pyrite oxidation and result in drainage with high concentrations of iron, manganese, and aluminum, as well as SO_4, Ca, Mg, K and Na. The concentrations of iron, manganese, and aluminum are generally very low in natural waters (< 1 mg/L) because of chemical and biological processes that cause their precipitation in surface water environments. The same chemical and biological processes remove iron, manganese, and aluminum from contaminated coal mine drainage, but the metal loadings from abandoned mine sites are often so high that the deleterious effects of these elements persist long enough to result in the pollution of receiving waters.

Passive treatment systems function by retaining contaminated mine water long enough to decrease contaminant concentrations to acceptable levels. The chemical and biological processes that remove contaminants vary among metals and are affected by the mine water pH and oxidation-reduction potential (Eh). Efficient passive treatment systems create conditions that promote the processes that most rapidly remove target contaminants. Thus, the design of passive treatment systems must be based on a solid understanding of mine drainage chemistry and how different passive technologies affect this chemistry.

Reduction

Chemical and microbial processes in anaerobic environments differ from those observed in aerobic environments. Because oxygen is absent, Fe^{2+} and Mn^{2+} do not oxidize, and oxyhydroxide precipitates do not form. Hydroxides of the reduced iron and manganese ions, $Fe(OH)_2$ and $Mn(OH)_2$, do not form because of their high solubility under acidic or circumneutral conditions. In passive treatment systems where mine water flows through anaerobic environments, its chemistry is affected by chemical and biological processes that generate bicarbonate and hydrogen sulfide.

Bacterial sulfate reduction not only improves water quality by the addition of bicarbonate alkalinity, it can also lower the concentrations of dissolved metals, M^{2+}, (e.g., Fe^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}) by precipitating them as metal sulfide solids.

$$M^{2+} + H_2S + HCO_3^- \rightarrow MS + 2H_2O + 2CO_2 \qquad \text{(O)}$$

For iron, the formation of iron monosulfide and even pyrite is possible:

$$Fe^{2+} + H_2S + S^0 \rightarrow FeS_2 + 2H^+ \qquad \text{(P)}$$

The removal of dissolved metals as sulfide compounds depends on pH, the solubility product of the specific metal sulfide, and the concentrations of the reactants. The solubilities of various metal sulfides are shown in Table 7 (Ehrlich 1981). Laboratory studies have verified that metal removal from mine water subjected to inflows of hydrogen sulfide occurs on an order consistent with the solubility products shown in this table (Hammack et al. 1993). The first metal sulfide that forms is CuS, followed by PbS, ZnS, and CdS. FeS is one of the last metal sulfides to form. MnS is the most soluble metal sulfide shown, and is not expected to form. Because of the low solubility of some of these metal sulfides relative to their solubilities as oxides or hydroxides, sulfate reduction can be an important process to lower some metal concentrations to acceptable levels, particularly for treating metal mine drainage.

Table 7. Solubility Products of Selected Metal Sulfides

Metal Sulfide	Solubility Product
CuS	4.0×10^{-38}
PbS	1.0×10^{-29}
ZnS	4.5×10^{-24}
CdS	1.4×10^{-23}
NiS	3.0×10^{-21}
FeS	1.0×10^{-19}
MnS	5.6×10^{-16}

For coal mine drainage, where metal contamination is generally limited to iron , manganese , and aluminum, the hydrogen sulfide produced by bacterial sulfate reduction primarily affects dissolved iron concentrations. Aluminum does not form any sulfide compounds in wetland environments, and the relatively high solubility of MnS makes its formation unlikely.

The precipitation of metal sulfides in an organic substrate improves water quality by decreasing mineral acidity without causing a parallel increase in proton acidity. Proton-releasing aspects of the H_2S dissociation process ($H_2S \rightarrow 2H^+ + S^{2-}$) are neutralized by an equal release of bicarbonate during sulfate reduction. An organic substrate in which 100 percent of the H_2S (produced by sulfate reduction precipitated as FeS) would have no effect on the mine water pH or alkalinity (although acidity would decrease). In fact, however, the chemistry of pore water in wetlands constructed with an organic substrate characteristically has pH 6 to 8 and is highly alkaline (Hedin et al. 1988, McIntire and Edenborn 1990). These alkaline conditions result, in part, from reactions involving hydrogen sulfide that result in the net generation of bicarbonate. Hydrogen sulfide is a very reactive compound that can undergo a variety of reactions in a constructed wetland. In most wetlands (constructed and natural), surface waters are aerobic while the underlying pore waters in contact with organic substrate are anaerobic. When sulfidic pore waters diffuse from the organic substrate into zones that contain dissolved ferric iron, dissolved oxygen, or precipitated ironand manganese oxides, the hydrogen sulfide can be oxidized. These reactions affect the mineral acidity and the alkalinity in various manners.

Metal Oxidation and Hydrolysis

Oxidation and hydrolysis reactions commonly cause concentrations of Fe^{2+}, Fe^{3+}, manganese , and Al to decrease when mine water flows through an aerobic environment. Whether these reactions occur quickly enough to lower metal concentrations to an acceptable level depends on the availability of oxygen for oxidation reactions, the pH of the water, the activity of microbial and/or other catalysts and inhibitors, and the retention time of water in the treatment system. The pH is an especially important parameter because it influences both the solubility of metal hydroxide precipitates and the kinetics of the oxidation and hydrolysis processes. The relationship between pH and metal-removal processes in passive treatment systems is complex because it differs among metals and also between abiotic and biotic processes.

The stoichiometries of the major metal removing reactions in passive treatment systems are:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (Q)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad (R)$$

$$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 + 2H^+ \qquad (S)$$

$$Mn^{2+} + 0.25O_2 + 1.5H_2O \rightarrow MnOOH + 2H^+ \qquad (T)$$

The first two (Q and R) are simple hydrolysis reactions, which require only the presence of water (and enough alkalinity to neutralize the H^+ produced). The last two reactions (S and T) require the presence of oxygen to oxidize the metal prior to hydrolysis. All of the reactions produce acidity, which was discussed previously. The goal of passive treatment systems is to drive these reactions to completion and collect the resulting solids before the water enters a receiving stream.

Iron

The most common contaminant of coal mine drainage is ferrous iron. In oxidizing environments common to most surface waters, ferrous iron is oxidized to ferric iron (reaction S). Ferrous iron oxidation occurs both abiotically and as a result of bacterial activity. The stoichiometry of the reaction is the same for both oxidation processes.

From the stoichiometry, it can be seen that one mole of oxygen can oxidize 4 moles of Fe^{2+}. This corresponds to 7.0 mg of Fe^{2+} oxidized per mg of O_2. The solubility of oxygen in water depends on both pressure and temperature. It can be as high as 13 mg/L (1 atm., < 5 ^{o}C) but under field conditions, a maximum practical DO level of 8 mg/L is a better estimate. At this oxygen concentration, only about 55 mg/L of Fe^{2+} can be oxidized without providing for additional oxygenation of the water.

Because the net result of the oxidation and hydrolysis process is the production of protons, the process can decrease pH. Thus, natural or constructed wetlands receiving circumneutral net acidic water commonly decrease both iron concentrations and pH. An example of this phenomenon is shown in Figure 2a. As water flowed through the constructed wetland, dissolved iron concentrations decreased from 95 mg/L to 15 mg/L, and pH decreased from 5.5 to 3.2. Figure 2b shows iron concentrations and pH in a wetland that received mine water with a net alkalinity. Despite the removal of 60 mg/L Fe^{2+} and the production of enough protons to theoretically lower the pH to 2.7, the pH did not decrease because bicarbonate alkalinity neutralized the proton acidity.

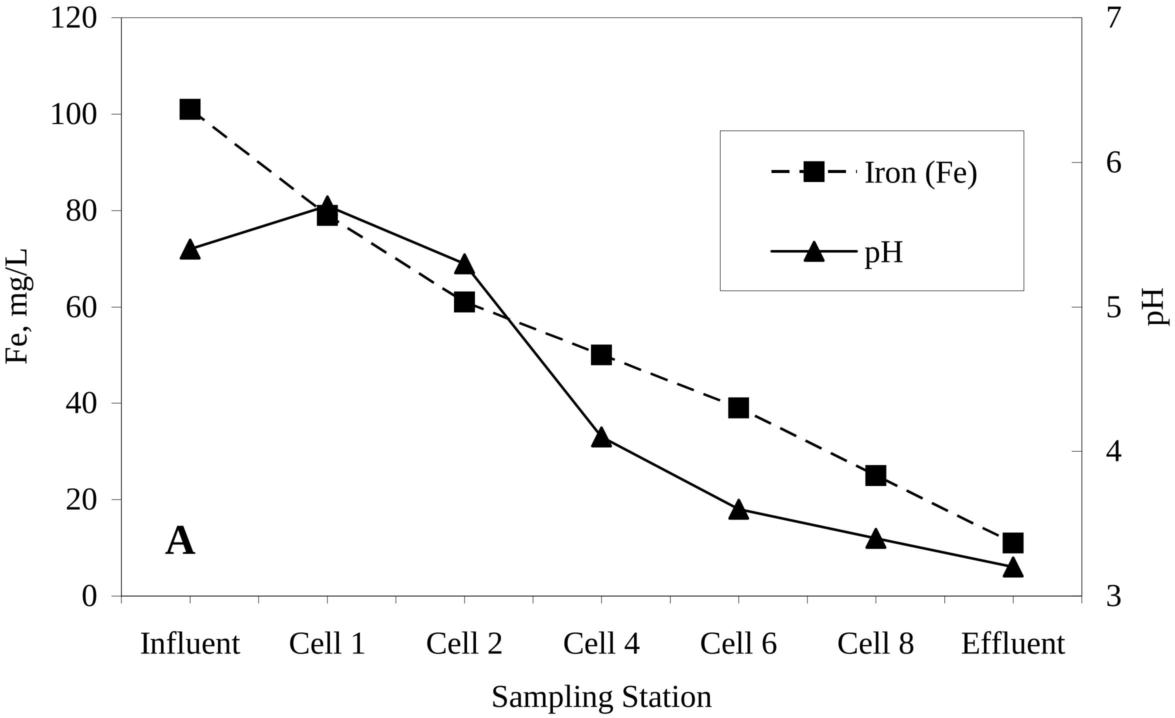

Figure 2a. Concentration of Iron and Field pH at the Emlenton Constructed Wetlands, which Receives Net Acidic Water

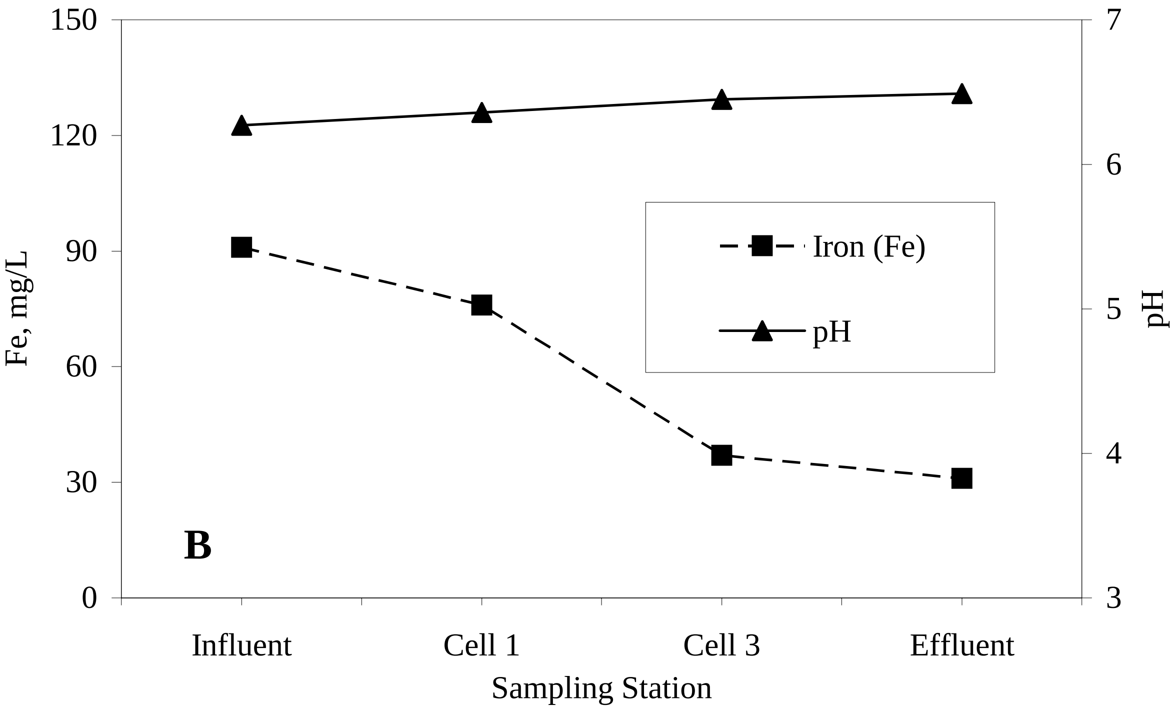

Figure 2b. Concentration of Iron and Field pH at Cedar Grove Constructed Wetlands which Receives Net Alkaline Water

As ferrous iron is converted to ferric iron, it is subject to hydrolysis reactions that can precipitate it as a hydroxide (reaction Q). The hydrolysis reaction occurs abiotically; catalysis of the reaction by microorganisms has not been demonstrated. Under equilibrium conditions, the solubility of the ferric hydroxide solid is very low and little dissolved ferric iron (< 1 mg/L) is predicted to exist, unless the pH of the water is less than 2.5. However, the rate of the hydrolysis reaction is also pH dependent, and significant Fe^{3+} can be found in mine water with a pH above 2.5. Figure 3 shows ferric iron concentrations for over 150 coal mine discharges. Significant dissolved ferric iron is not generally present, unless the pH is less than 4. The highest concentrations of ferric iron occurred when the pH is less than 3.

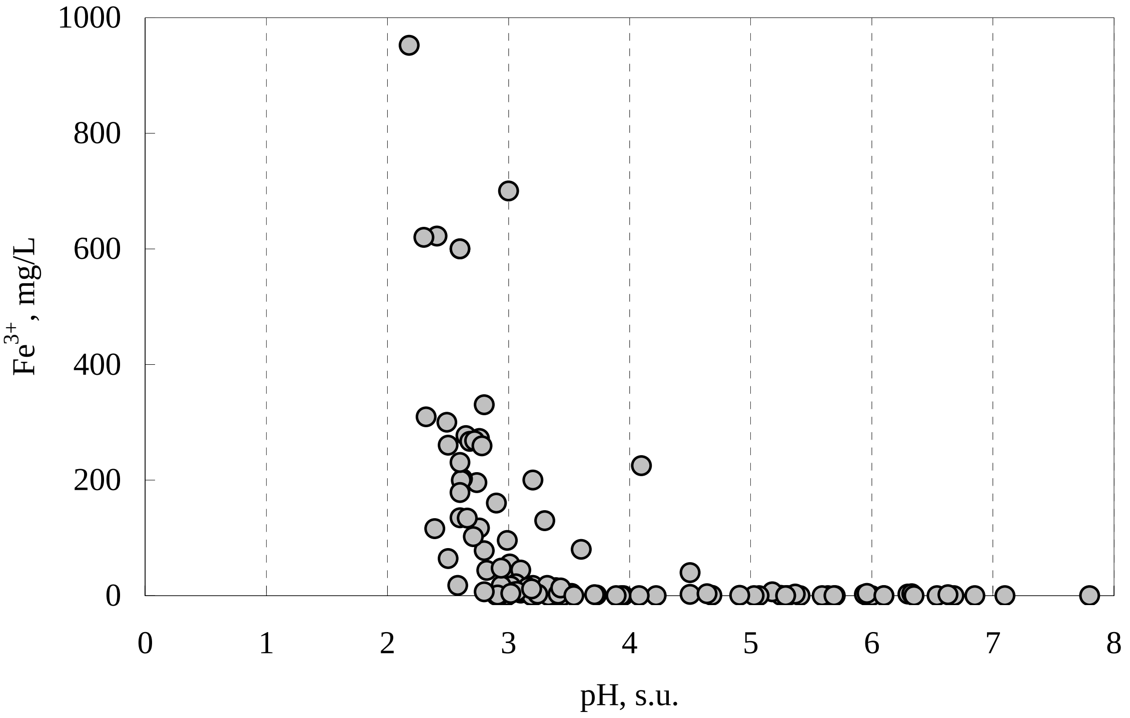

Figure 3. Dissolved Ferric Iron Concentration Versus pH in Coal Mine Discharge

Reaction rates are less well understood than stoichiometry and solubility. For the two rates of importance to iron oxidation and hydrolysis, the oxidation rate is usually the slowest. Metal hydrolysis reactions are much faster than oxidation reactions, and can be ignored at all but the lowest pH values. At low pH values, Singer and Stumm (1970a) suggested a fourth-order relationship with pH, which indicated that ferric iron hydrolysis processes shift from a very rapid rate at pH greater than 3, to a very slow rate at pH less than 2.5.

Metal oxidation can be influenced by a number of factors that can accelerate (catalyze) or retard (inhibit) the rate. In the simplest case where possible biological, catalytic, and inhibitory mechanisms are ignored, the rate of ferrous iron oxidation can be described by equation 3.

$$d\,[\mathrm{Fe(II)}] / dt = -k\,[\mathrm{Fe(II)}]\,[O_2]\,[H^+]^{-2} \qquad (3)$$

As can be seen from the inverse second order dependence on $[H^+]$, the pH of the mine water dramatically affects the kinetics of the oxidation process (Singer and Stumm 1970a, Singer and Stumm 1970b). When oxygen is not limiting, the rate of homogenous abiotic iron oxidation slows a hundredfold for every unit decrease in pH. At pH values greater than 8, the process is fast (rates are measured in seconds), while at pH values less than 5, the process is slow (rates are measured in days). The presence of bicarbonate alkalinity buffers mine water at a pH of 6 to 7, a range at which homogeneous abiotic iron oxidation processes should dominate.

The effect that pH can have on the mechanism of iron oxidation is shown by the data in Figure 4. Samples were collected from two mine drainages that were both contaminated with ferrous iron but had different pH and alkalinity values. The samples were returned to the laboratory and exposed to aerobic conditions. For the circumneutral waters, oxidation of ferrous iron occurred at a rate of 18 mg $L^{-1}\,hr^{-1}$, while the rate for the raw acidic samples was only 1.4 mg $L^{-1}\,hr^{-1}$. In order to evaluate the significance of bacterial processes in iron oxidation, splits of both samples were filter-sterilized (0.22 µm membrane filter) before the experiment was begun. Removal of bacteria had no effect on the oxidation of ferrous iron for the circumneutral water, but completely inhibited ferrous iron oxidation for the acidic water.

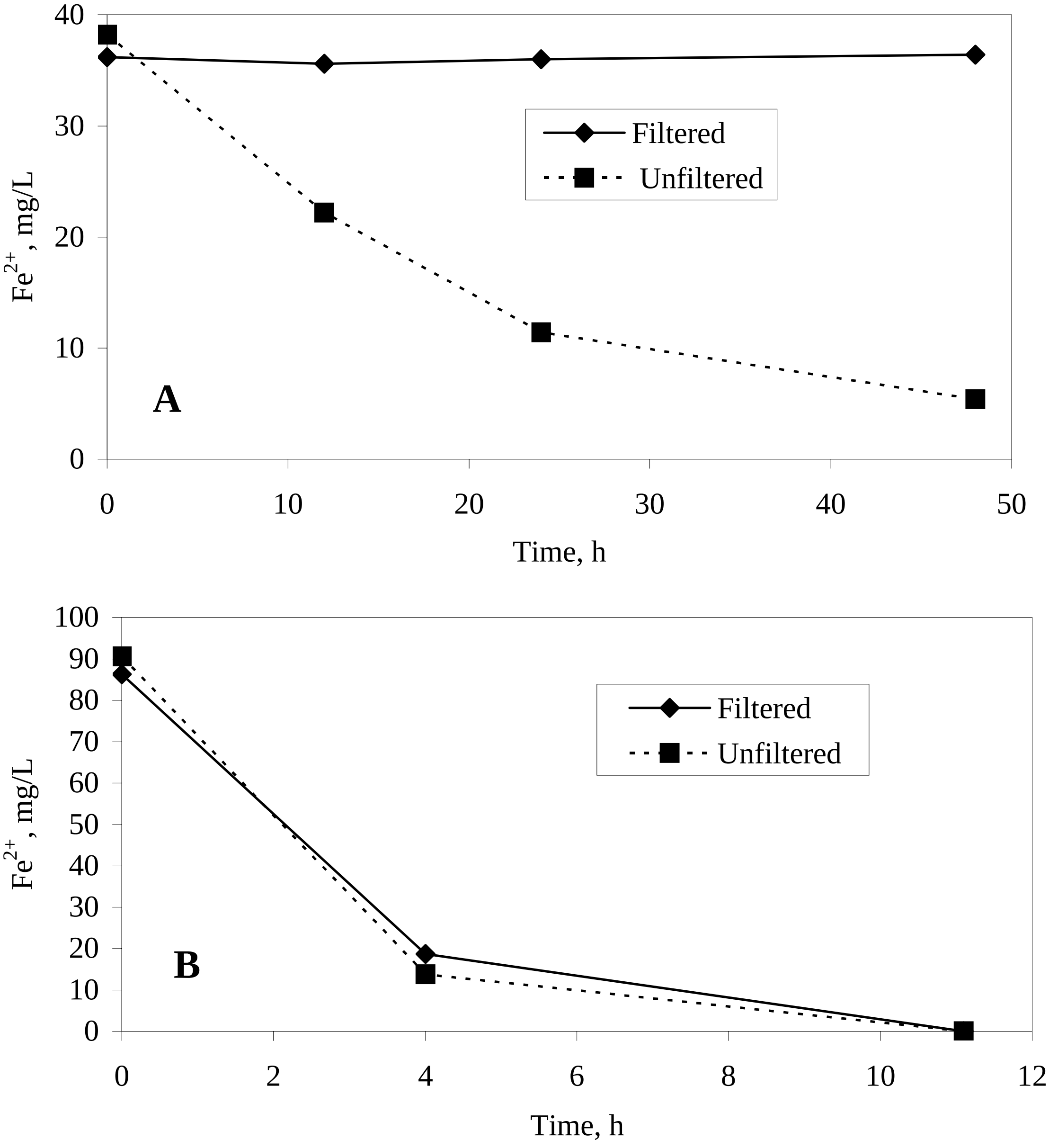

Figure 4. Removal of Ferrous Iron from Acidic and Alkaline Mine Waters in a Laboratory Experiment

Untreated mine drainage was collected from the (A) acidic Latrobe site and (B) alkaline Cedar Grove site. Splits of each sample were filter sterilized (0.22 micrometer filter).

In contrast to the uncatalyzed chemical rate, bacterial oxidation of ferrous iron peaks at pH values between 2 and 3, while very little activity occurs at pH values greater than 5 (Nealson 1983a). Waters containing no alkalinity have a pH less than 4.5, and the removal of iron under oxidizing conditions occurs primarily by bacterial oxidation, accompanied by hydrolysis and precipitation (Kirby et al. 1999). Equation 4 gives the rate of loss of ferrous iron via the microbial mechanism. Note that in the microbial case, the rate is directly proportional to the hydrogen ion concentration and contains a term to account for the number of bacteria present, [*Bact*].

$$d\,[\mathrm{Fe(II)}] / d\mathrm{t} = -\,k_{\mathrm{bio}}\,[Bact]\,[\mathrm{H}^+]\,[\mathrm{Fe(II)}]\,[\mathrm{O}_2] \tag{4}$$

Solid surfaces, in particular the hydrous ferric oxide surface itself, can catalyze the oxidation of ferrous iron that adsorbs to its surface. There have been recent attempts to exploit this mechanism in a recirculated iron oxide reactor in an effort to increase iron removal rates over those obtained in conventional ponds and wetlands (Dietz and Dempsey 2001). The rate of heterogeneous catalysis is given in equation 5. In this case, the rate expression contains a term to account for the amount of oxide present, [Fe(III)], and is proportional to the inverse of the hydrogen ion concentration.

$$d\,[\mathrm{Fe(II)}] / d\mathrm{t} = -\,k_{\mathrm{hetero}}\,[\mathrm{Fe(III)}][\mathrm{Fe(II)}]\,[\mathrm{O}_2]\,[\mathrm{H}^+]^{-1} \tag{5}$$

Kirby and Elder Brady (1998) list several other factors that have been reported to affect Fe(II) oxidation rate in natural waters: Cu(II), Co(II), anions that form complexes with Fe(III), organic acids, Na^+, presence of ferric hydroxide solids, ionic strength, sulfate, light intensity, colloidal silica and aluminum oxide, and bentonite clay are all listed, together with literature citations to the original work. It is likely that except for the presence of ferric hydroxide solids, these other factors are not significant in passive treatment systems. Light intensity, which can influence iron photoreduction (McKnight et al. 2001) may be significant, but conflicting results (Wieder 1994) in the literature demonstrate that further study is needed.

Temperature is known to affect the rate in a number of ways. Because the dissociation constant for water, K_w, depends on temperature, this change must be taken into account during the conversion from pH, the measured parameter, to hydroxide ion concentration, the rate dependent variable. Alternatively, the rate constant can be determined using Equation 3 (often in the integrated form) with the realization that it contains K_w. However, because K_w changes with temperature, the former conversion of pH to $[\mathrm{OH}^-]$ is preferred when rate constants determined at different temperatures are to be used to determine an activation energy. The temperature affects the Henry's law constant, used to calculate the molar concentration of oxygen from its partial pressure. However, in many studies, the dissolved oxygen concentration is measured directly.

Rate constants increase with increasing temperature. To quantitatively model the iron loss in a system where the temperature is not constant, the temperature dependence is usually expressed as the exponential given in equation 6 (Kirby et al. 1999, Watzlaf et al. 2001).

$$\mathrm{k} = \mathrm{A}\,\mathrm{e}^{\frac{-E_{act}}{RT}} \tag{6}$$

Manganese

Manganese undergoes oxidation and hydrolysis reactions that result in the precipitation of manganese oxyhydroxides. The specific mechanism(s) of Mn^{2+} precipitation from aerobic mine water in the absence of chemical additions are uncertain. Mn^{2+} may be oxidized to either a +3 or a +4 valence, either one of which rapidly precipitates. (See reaction T.) If MnOOH precipitates over time it likely oxidizes to the more stable MnO_2. In alkaline environments, Mn^{2+} can precipitate as a carbonate (reaction U), which may be oxidized by oxygen to MnO_2 via reaction V (Diehl and Stumm 1984).

$$Mn^{2+} + HCO_3^{-} \rightarrow MnCO_3 + H^{+} \qquad (U)$$

$$MnCO_3 + 0.5O_2 \rightarrow MnO_2 + CO_2 \qquad (V)$$

Regardless of the mechanism by which Mn^{2+} is oxidized to Mn^{4+}, the removal of one mole of Mn^{2+} from solution results in the release of two moles of H^{+}, or an equivalent decrease in alkalinity (HCO_3^{-}).

The kinetics of Mn^{2+} oxidation reactions are strongly affected by pH. Abiotic oxidation reactions are very slow at pH less than 8 (Stumm and Morgan 1981). Microorganisms can catalyze Mn^{2+} oxidation, but their activity is limited to aerobic waters with pH greater than 6 (Nealson 1983b).

Although the hydrolysis of manganese produces protons, the precipitation of MnOOH does not result in large declines in pH, which can happen when FeOOH precipitates. This difference between manganese and iron chemistry is due to the fact that no natural mechanism exists to rapidly oxidize Mn^{2+} under acidic conditions. If pH falls below 6, Mn^{2+} oxidation virtually ceases, the proton-producing hydrolysis reaction ceases, and the pH stabilizes.

The oxidation and precipitation of Mn^{2+} from solution is accelerated by the presence of MnO_2 and FeOOH (Stumm and Morgan 1981, Davies and Morgan 1989). Both solids reportedly act as adsorption surfaces for Mn^{2+} and catalyze the oxidation mechanism. While additions of FeOOH to water containing manganese might accelerate manganese oxidation, the direct precipitation of FeOOH from mine water that contains Fe^{2+} does not generally stimulate manganese removal processes in passive treatment systems. Figure 5 shows that concentrations of manganese and iron in mine water markedly decreased as it flowed through a constructed wetland. On average, iron decreased from 150 mg/L to less than 1 mg/L, while manganese decreased from 42 mg/L to 11 mg/L. Removal of metals occurred sequentially, not simultaneously. Two-thirds of the decrease in iron concentration occurred between the first and second sampling stations. The wetland substrate in this area was covered with precipitated FeOOH, and the water was turbid with suspended FeOOH. Despite the presence of large quantities of FeOOH, little change occurred in the concentration of manganese between the first and second sampling station. The slight decrease in manganese that occurred was proportionally similar to the change in Mg, suggesting that dilution was the most likely cause of the decrease in manganese concentrations. Between stations 3 and 5, there was little iron present in the water and little visual evidence of FeOOH sludge on the wetland substrate. Most of the observed removal of manganese occurred in this iron-free zone.

The absence of simultaneous precipitation of dissolved iron and manganese from aerobic alkaline waters likely results from the reduction of oxidized forms of manganese by ferrous iron as shown in reaction W, or reaction X.

$$MnO_2 + 2Fe^{2+} + 2H_2O \rightarrow 2FeOOH + Mn^{2+} + 2H^{+} \qquad (W)$$

$$MnOOH + Fe^{2+} \rightarrow FeOOH + Mn^{2+} \qquad (X)$$

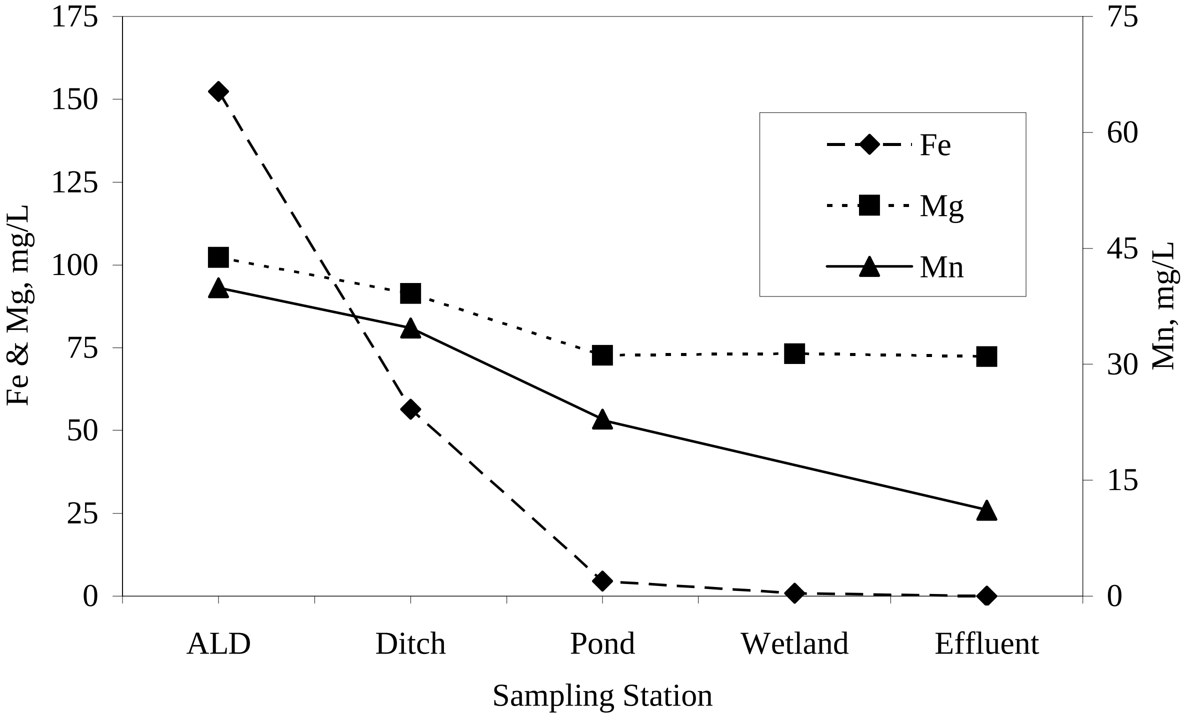

Figure 5. Mean Concentration of Iron, Manganese and Magnesium at the Morrison Wetland as the Mine Water Flows Linearly through the System

Figure 6 shows the results of a laboratory study that demonstrates the instability of manganese oxides in the presence of ferrous iron. Water samples and manganese oxides were collected from a wetland that removed iron and manganese in a sequential manner. The wetland influent was alkaline (pH 6.2, 162 mg/L alkalinity) and contaminated with 50 mg/L iron and 32 mg/L manganese . Two flasks of mine water received MnO_2 additions, while the controls did not receive MnO_2. Concentrations of dissolved iron and manganese were monitored in each flask over a 73-hour period. In all flasks, concentrations of iron decreased to less than 1 mg/L. In the control flasks, concentrations of iron decreased to less than 3 mg/L within 43 hours. In flasks that received MnO_2, concentrations of iron decreased to less than 3 mg/L in only 22 hours. No change in concentrations of manganese occurred in the control flasks. Concentrations of manganese in the MnO_2 flasks increased by 15 mg/L during the first 22 hours and did not change during the remaining 50 hours of the experiment. The association of accelerated precipitation of iron with solubilization of Mn^{2+} suggests that the MnO_2 oxidized Fe^{2+} in a manner analogous to reaction K.

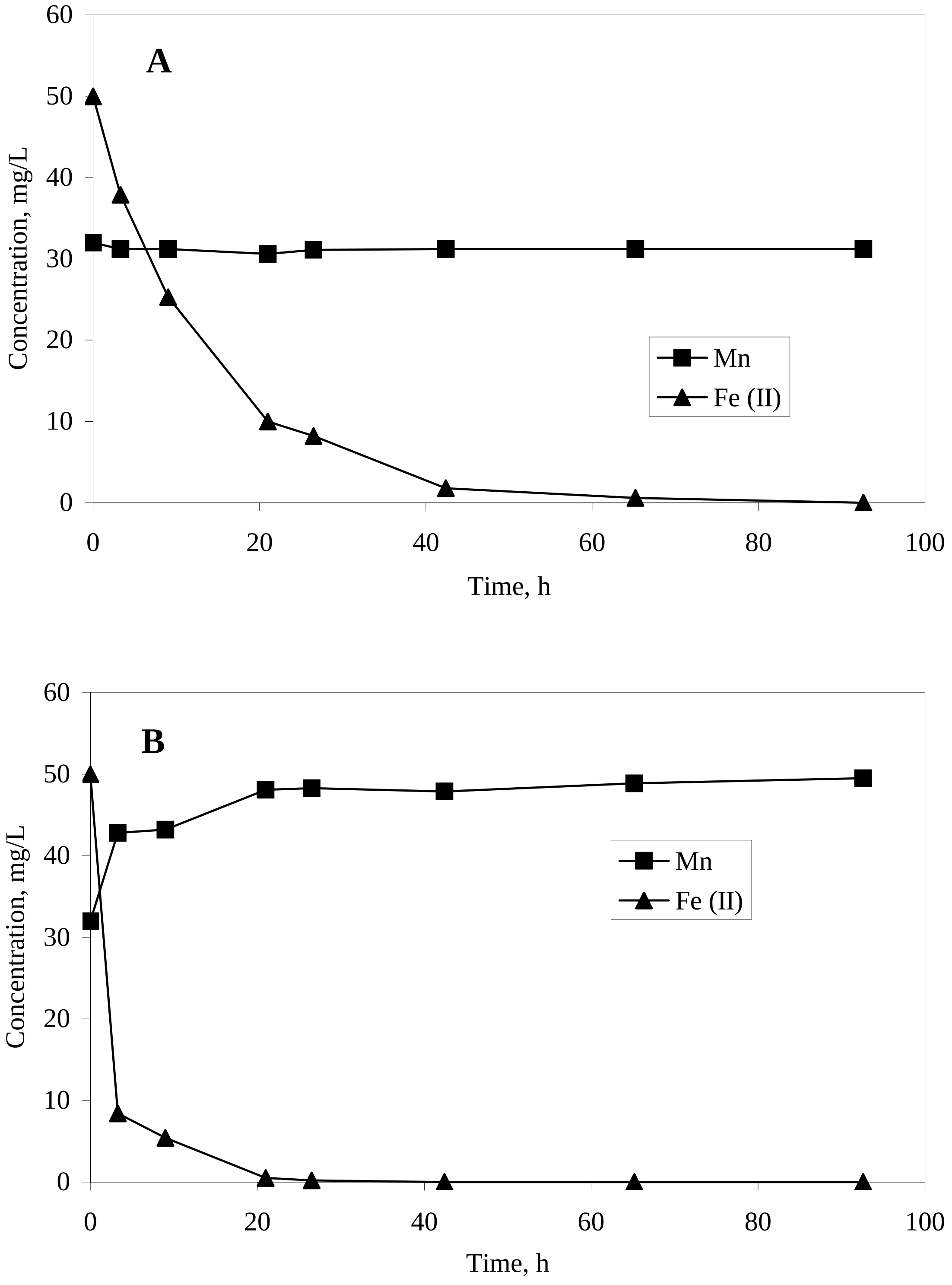

Figure 6. Changes in the Concentrations of Ferrous Iron and Manganese in (A) the Absence of the MnOOH and (B) the Presence of MnOOH

The data presented in Figure 5 and Figure 6 demonstrate important aspects of iron and manganese chemistry in passive treatment systems. Iron oxidizes and precipitates from alkaline mine water much more rapidly than manganese. One reason for the differences in kinetics is that the oxidized manganese solids are not stable in the presence of Fe^{2+}. Concentrations of ferrous iron must decrease to very low levels before Mn^{2+} oxidation processes can result in a stable solid precipitate. In the absence of Fe^{2+}, manganese removal is still a very slow process under laboratory conditions. Conditions in a wetland may either accelerate manganese removal reactions or promote mechanisms that are not simulated in simple laboratory experiments. However, both field and laboratory investigations indicate that, under aerobic conditions, the removal of manganese occurs at a much slower rate than the removal of iron.

Aluminum

Aluminum has only one oxidation state in aquatic systems, +3. Oxidation and reduction processes, which complicate iron and manganese chemistry, do not directly affect concentrations of dissolved aluminum. Instead, concentrations of aluminum in mine waters are primarily influenced by the solubility of $Al(OH)_3$ (Hem 1985, Nordstrom and Ball 1986). At pH levels between 5 and 8, $Al(OH)_3$ is insoluble, and concentrations of dissolved aluminum are usually less than 1 mg/L. At pH values less than 4, $Al(OH)_3$ is highly soluble and concentrations much higher than 2 mg/L are possible. The amount of aluminum found in over 150 different mine drainage samples are show in Figure 7. No significant amounts of dissolved aluminum were found above a pH of 4.5, consistent with the expected behavior, based on solubility. The kinetics of hydrolysis do not appear to play a role.

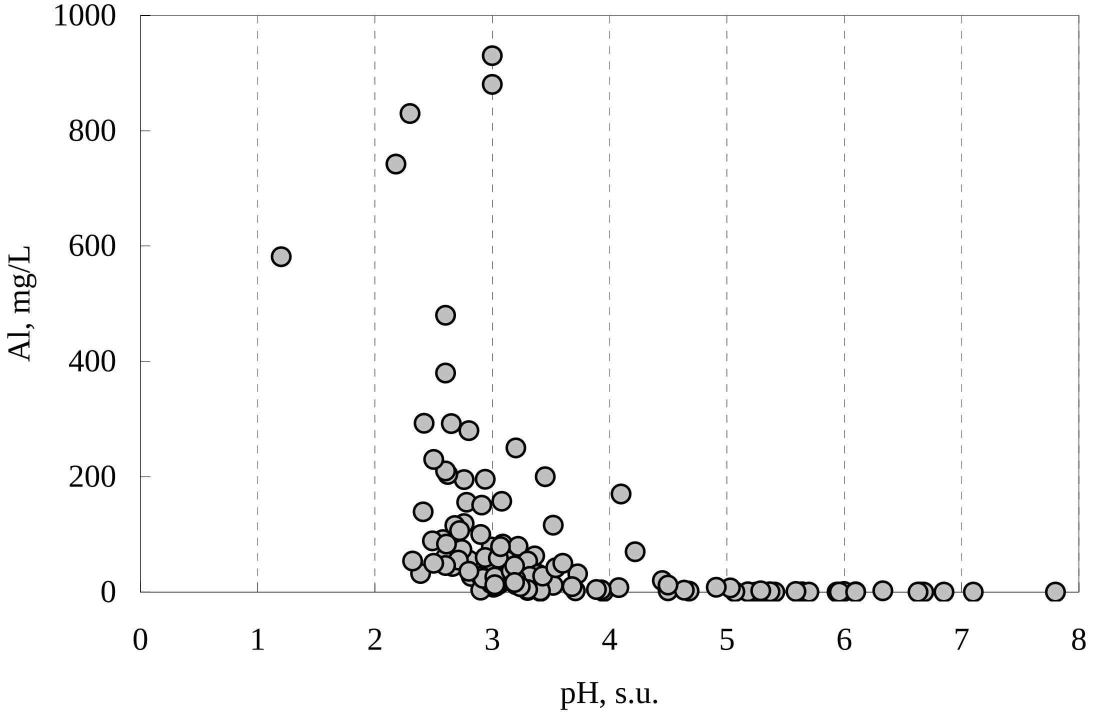

Figure 7. Dissolved Aluminum Concentration Versus pH in Coal Mine Discharges

The passage of mine water through highly oxidized or highly reduced environments has no effect on concentrations of aluminum unless the pH also changes. In those cases where the pH of mine water decreases (due to iron oxidation and hydrolysis), concentrations of aluminum can increase because of the dissolution of alumino-silicate clays by the acidic water. When acidic mine water passes through anaerobic environments, the increased pH that can result from carbonate dissolution or microbial activity can cause the precipitation of $Al(OH)_3$. In addition to $Al(OH)_3$, aluminum hydroxysulfate minerals can form when the drainage contains aluminum and SO_4^{2-} at pH levels greater than 4.3 (Nordstrom and Ball 1986).

Robbins et al. (1996) found poorly crystalline aluminite $[Al_2(SO_4)(OH)_4 \cdot 7H_2O]$ in an ALD in West Virginia.

Materials and Methods

Collection of Water Samples

Water samples were collected at passive treatment systems from their influent and effluent points, and, if applicable, between unit operations within the system. Raw and acidified (1 to 2 mL of concentrated HCl) water samples were collected in 125 to 250 mL plastic bottles at each sampling point. Acid was added to lower the pH to below 1.0. At sites where particulates were visible in water samples, an additional sample was collected that was filtered through a 0.2 µm membrane filter prior to acidification. Samples were refrigerated in the analytical laboratory at 4°C until analysis. Measurements of pH and temperature were made in the field with a calibrated portable pH/ISE meter. Alkalinity was measured in the field using a pH meter and an Orion Total Alkalinity Test Kit or a Hach Digital Titrator.

Analysis of Water Samples

Concentrations of iron, manganese, aluminum, calcium, magnesium, sodium, cobalt, nickel, and zinc were determined in the acidified samples using Inductively-Coupled Argon Plasma-Atomic Emission Spectroscopy (ICAP-AES) (Instrumentation Laboratory Plasma 100 model or TJA Polyscan 61E). The acidified samples were at times filtered through a 0.45 µm membrane filter to prevent clogging of the small diameter tubing in the system.

Ferrous iron concentrations were determined on acidified samples by the potassium dichromate method (Fales and Kenny 1940). Sulfate concentrations were determined by one of three methods: (1) reaction with barium chloride after first passing the raw sample through a cation exchange resin with Thorin used as the end-point indicator (Kleinmann et al. 1988), (2) ion chromatography, or (3) ICP-AES. The agreement among these methods was found to be very good (within ~2 percent).

Acidity was determined by adding H_2O_2, heating and titrating the solution with NaOH (American Public Health Assoc. 1985). An auto titrator was used to determine the inflection point in the titration curve (i.e., first derivative mode). Acidity and alkalinity are reported as mg/L $CaCO_3$ equivalent.

For each set of samples for a particular site, a duplicate, standard, and spike were analyzed for quality control purposes. The relative standard deviation for duplicates were less than 5 percent. Recovery for the standards were within 3 percent of the original standard. Spike recoveries were within 5 percent of the expected values.

Flow Rate Measurements

Water flow rates were determined by one of three methods. Whenever possible, flow was determined by the time necessary to collect a known volume of water using a bucket and stopwatch. In all cases, three to five measurements were made at each sampling location, and the mean flow rate of these measurements was reported. Flows were also measured with permanently installed calibrated flumes, and portable calibrated pipe weirs.

Analysis of Iron Sludge

A sample of iron sludge was collected at the Morrison II site. Sludge at this site was selected as a representative of iron sludge precipitated under alkaline conditions. Approximately 60 cm^3 of sludge was collected with a spatula and allowed to "drip dry" for about 1 minute before placing it in a 125-mL plastic bottle. After transport back to the laboratory, it remained undisturbed for about 6 weeks. The supernatant liquid was then withdrawn by pipette from the top of the sludge (approximately 15 percent of the total volume). A graduated cylinder was filled with 8.0 mL of distilled, deionized water. Sludge was added to the water until it rose to the 10.0 mL level, thereby collecting 2.0 cm^3 of sludge. The sludge/water mixture was transferred into a volumetric flask, and nitric and hydrochloric acid were added to totally dissolve the sludge. Distilled, deionized water was added, resulting in a final volume of 1.0 L. A portion of this solution was analyzed for metal content as outlined above. It was found that this sludge contained 0.17 grams of iron per cm^3 of sludge. This is consistent with previous measurements of sludges precipitated from alkaline waters at other sites, and can be used to calculate how fast systems will fill with iron precipitates.

Removal of Contaminants by Passive Unit Operations

Aerobic Wetlands and Ponds

To make reliable evaluations of wetland performance, a measure should be used that allows comparison of contaminant removal between systems that vary in size and the chemical composition and the flow rate of mine water they receive. In the past, concentration efficiency (CE%) was a common measure of performance (Girts et al. 1987, Weider 1989). Using iron concentration as an example, the calculation was:

$$CE\% = [(Fe_{in} - Fe_{eff})/Fe_{in}] \times 100 \tag{7}$$

where the subscripts "in" and "eff" represented wetland influent and effluent sampling stations, and iron concentrations were in mg/L.

Except in carefully controlled environments, concentration efficiency is a very poor measure of wetland performance. The efficiency calculation results in the same measure of performance for a system that lowers iron concentrations from 300 mg/L to 100 mg/L as one that lowers concentrations from 3 mg/L to 1 mg/L. Neither the flow rate of the drainage nor the size of the treatment system is incorporated into the calculation. As a result, the performance of systems are compared without accounting for differences in flow rate (which vary from < 10 L/min to > 1,000 L/min), or for differences in system size (which vary from < 0.1 ha to > 10 ha) (Weider 1989).

A more appropriate method for measuring the performance of treatment systems calculates contaminant removal from a loading perspective. The daily load of contaminant received by a wetland is calculated from the product of concentration and flow rate data. For iron, the calculation of load in grams per day is:

$$Fe_{in}\ (g/d) = 1.44 \times flow\ (L/min) \times Fe_{in}\ (mg/L) \tag{8}$$

where 1.44 is the unit conversion factor to convert minutes to days, and milligrams to grams.

The daily mass of iron removed by the wetland between two sampling stations,

$Fe(g/d)_{rem}$, is calculated by comparing contaminant loadings at the two points.

$$Fe_{rem}\ (g/d) = Fe_{in}\ (g/d) - Fe_{eff}\ (g/d) \qquad (9)$$

An area-adjusted daily iron removal rate is then calculated by dividing the load removed by the surface area of the treatment system lying between the sampling points.

$$Fe_{rem}\ (g\ d^{-1}\ m^{-2}) = Fe_{rem}\ (g/d)/SA\ (m^2) \qquad (10)$$

Using this area-adjusted removal rate as the measure of treatment performance, Hedin et al. (1994a) reported typical removal rates of 10 to 20 g d^{-1} m^{-2} for iron, and 0.5 to 1.0 g d^{-1} m^{-2} for manganese.

More recently, several groups have attempted to develop models that will more effectively estimate the performance of treatment systems, especially for iron removal. Watzlaf et al. (2001) were able to model a system consisting of an aerobic pond, an aeration cascade, and a wetland using only equations 3 and 6. They found that the overall performance and the performance of certain sections of the system fell within the 10 to 20 g d^{-1} m^{-2} range, but that some sections did not. The model indicated that the pH was limiting the rate of removal.

Kirby et al. (1999) used a combination of the abiotic rate expression (equation 3), the biological rate expression (equation 4), and the temperature dependence (equation 6) to model a set of 17 ponds. They found that the relative importance of the biotic and abiotic mechanisms was determined mainly by pH, with the abiotic path predominating at the higher pH values. They suggest that pH and temperature are the most important variables for determining iron oxidation rates, and therefore, iron removal rates. Little can be done to control temperature in a passive treatment. The Kirby et al. (1999) work suggests that increasing pH from 6.1 to 6.4, for example, greatly enhances oxidation, whereas doubling dissolved oxygen (as long as oxygen is sufficiently high stoichiometrically to oxidize metals), pond volume, or retention time has considerable less impact on oxidation rates.

Dempsey et al. (2001) modeled seasonal fluctuations of two systems using a combination of the homogeneous rate (equation 3) and the heterogeneous rate (equation 5). They found that oxygen transfer was rate limiting in one system, and that the amount of catalytic reaction provided by ferric hydroxides was the determining factor at the second site. While heterogeneous catalysis apparently plays a significant role in iron oxidation, it is difficult to increase concentrations of iron solids in a completely passive system. Such catalysis could be quite important in semi-passive or active treatment systems.

No one has yet tried a combination of all three rate expressions to apportion the relative importance of the three mechanisms at a given site, but such studies are undoubtedly underway. Because the three rate expressions contain different parameters (bacteria, ferric oxides) and have different dependencies on the pH, it should be possible, in principle, to differentiate among the three mechanisms.

It appears that the original estimate of Hedin et al. (1994a) of 10 to 20 g d^{-1} m^{-2} remains a convenient pre-construction rule-of-thumb for estimating pond and wetlands sizes. Studies undertaken since the publication of Hedin guidelines tend to support them in the majority of cases (Younger et al. 2002).

Anoxic Limestone Drains

All sites are located in western Pennsylvania, with the exception of the Elklick site, which is located in northwestern Maryland. Discharges are associated with Allegheny group coals (mainly the Kittanning and Clarion seams) formed during the Pennsylvanian period.

Site Descriptions

Howe Bridge 1 - Mine pool discharge, which occurs through an abandoned gas well, is captured and piped to the ALD. Influent water is sampled via a well prior to contact with limestone. Four sampling wells are evenly spaced along the length of the drain.

Howe Bridge 2 - Mine pool discharge, which occurs through an abandoned gas well, is treated in an S-shaped ALD. Influent water is sampled via a well as the water flows into the beginning of the ALD. Two sampling wells are located along the length of the ALD.

Morrison - Seepage is intercepted at the toe of the spoil of a reclaimed surface mine. After the ALD was built, another seep, similar in quality to the pre-construction water, was discovered, and is being used to represent influent water quality. Two sampling wells are located along the length of the ALD.

Filson (R and L) - Seepage is intercepted at the toe of the spoil. A seep, located between the ALDs that is similar in quality to the pre-construction raw water, is used to represent influent water quality.

Elklick -Water from an abandoned borehole is collected in a bed (7.0 m x 1.8 m x 0.9 m) of crushed, low-pyrite sandstone at the head of the ALD. Influent water is sampled at a well located in this sandstone. Three sampling wells are equally spaced along the length of the ALD.

REM (R and L) and Schnepp - ALDs were constructed down slope from collapsed underground mine entrances. Influent water quality is based on historical data, which may overestimate contaminant levels, since water quality elsewhere in the watershed has improved significantly over the past decade.

Jennings - An abandoned underground mine discharge was collected in a French drain filled with inert river gravel and piped to the system. Influent water was sampled prior to contact with limestone via a sampling well. The ALD consisted of a series of 6 buried limestone cells. Water flowed into the bottom of each cell and exited through the top before being piped to the next cell.

Detention times (t_d) were calculated based on ALD volume (V) and average flow (Q), using $t_d = 0.49V/Q$. The porosity value was determined using containers of known volume filled with the limestone used in the ALDs. The amount of water it took to fill these limestone-filled containers to the top of the limestone was measured. An average value of 49 percent for porosity was obtained. To confirm these calculated detention times, tracer tests were conducted at two ALDs. The results of these tests are presented below. Additional details on the construction of each ALD are presented in Table 8.

Table 8. Dimensions, Stone Size and Quality, and Source of Influent Water Quality Data for ALDs

ALD Site	**ALD Dimensions: Length x Width x Depth, meters**			**Limestone**		**Influent Water Quality Data Source**
				size, cm	**% $CaCO_3$**	
Howe Bridge 1	36.6	6.1	1.2	5.1 - 7.6	82	Well
Howe Bridge 2	13.7	4.6	0.9	5.1 - 7.6	82	Well
Elklick	36.6	3.1	0.9	5.1 - 20.3	85	Well
Jennings[1]	228	1.0	1.0	15.2	90	Well
Morrison	45.7	0.9	0.9	5.1 - 7.6	92	Adjacent Seep
Filson - R	54.9	6.1	0.9	5.1 - 7.6	88	Adjacent Seep
Filson - L	54.9	6.1	0.9	5.1 - 7.6	88	Adjacent Seep
Schnepp	12.2	6.1	0.9	1.9 - 2.5	90	Historical
REM - R	13.7	7.6	0.9	7.6	82	Historical
REM - L	61.0	16.8	0.9	7.6	82	Historical

[1] *The Jennings ALD is composed of 6 sequential cells, each cell approximately 38 m x 1 m x 1 m.*

Tracer Studies

To obtain information about the flow characteristics within the ALDs, tracer studies were undertaken at two of the sites. Known amounts of concentrated sodium bromide solutions were added to the influent flow. Samples were collected at the effluent after selected periodic intervals (1to 8 hrs) using automatic samplers. Bromide concentrations were measured using a specific ion electrode (in the field), and by ion chromatography (samples returned to lab) with suppressed conductivity detection using a standard anion column. In analyzing the tracer data, the effective (or mean) detention time (t_e) was calculated by $t_e = \Sigma[(C_t\ t)\Delta t]/E(C_t\ \Delta t)$, where C_t is the bromide concentration at time t, t is the time after tracer addition, and Δt is the time between samples.

The concentration profile obtained at the Howe Bridge site is shown in Figure 8. The second experiment at the Morrison site, produced a similar profile. The profiles are asymmetrical with rapidly rising concentrations at shorter times and gradually dropping concentrations at longer times. Such profiles may be the result of a number of factors, such as diffusion, channeling, back-mixing, adsorption, and mobile phase saturation, acting simultaneously. In the case of ALDs, the first three factors presumably predominate.

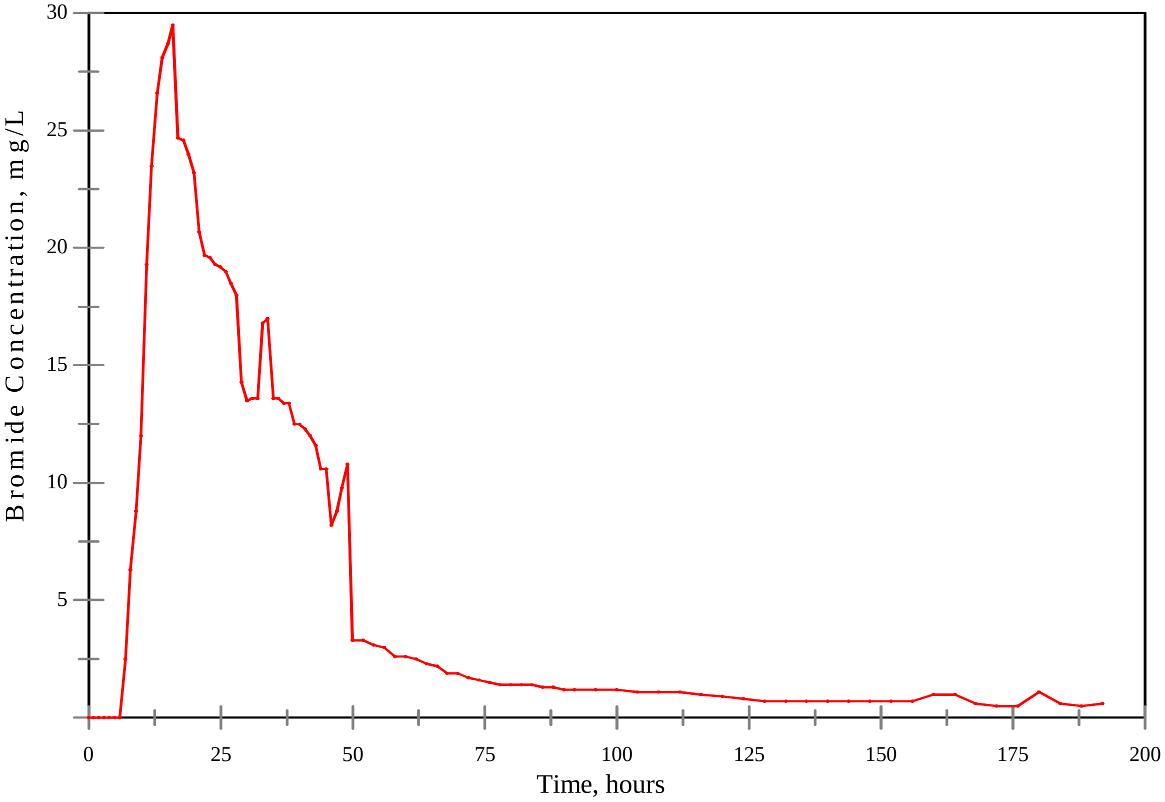

Figure 8. Bromide Concentration Versus Time in the Effluent of the Howe Bridge ALD 1 Resulting from a Pulse Input of a Bromide Tracer

In Table 9, a number of descriptive statistics that can be used to characterize the flow are compared to the detention time calculated using the drain volume and the aforementioned 49 percent void volume. In both cases, the maximum concentration occurred fairly soon after the first appearance of the bromide in the effluent. The time required for 50 percent of the material to exit the drain—the median detention time—was considerably longer than the time to peak, and most closely matched the calculated detention time. The time-weighted average—(i.e, mean, or effective) —detention time was longer yet. Of these statistics, we consider the median detention time to be the better measure of performance for ALDs. The ratio of the median (50 percent eluted) to the mean (effective) detention time is less than one. This indicates that a disproportionate amount of material is eluting at times earlier than expected for an ideally behaving plug-flow system, and is interpreted as an indication of channeling (i.e., short-circuiting). In addition, concentrations of bromide above background levels continued to be measured in ALD effluent for several days after tracer addition, indicating that more material is eluting at times longer than would be ideally expected. This is taken as an indication that back-mixing or dead areas exist within the drain. Thus, the ALDs appear to provide both shorter and longer detention times than would be expected, based on simple plug-flow. Channeling is of concern because it leads to inefficiencies in calcite dissolution. The longer residence times of some of the mine water is not necessarily beneficial, because the concentration of alkalinity in this water does not increase significantly after 15 hours of contact with the limestone.

Table 9. Tracer Test Data for Two ALDs

ALD	**Howe Bridge 1**	**Morrison**
Time to first appearance, hrs	7	4
Time to peak, hrs	16	10
Time for 50% of tracer to elute, hrs	30	61
Effective detention time1, hrs	40	87
Calculated detention time2, hrs	25	47

[1] *Effective detention time (t_e) calculated by $t_e = \Sigma[(C_t\ t)\Delta t]/E(C_t\ \Delta t)$, where C_t = bromide concentration at time t, t = time after tracer addition, and Δt = time between samples.* [2] *Calculated detention time (t_d), based on limestone volume (V) and average flow rates (Q) by $t_d = 0.49V/Q$, using 49% for porosity.*

Limestone Dissolution and Alkalinity Production

Tables 8 through 12 show data describing the 10 ALDs discussed in this report. These ALDs intercept flows ranging from about 10 to about 100 L/min. When possible, ALDs were designed to provide a detention time of at least 15 hours. The importance of detention time is seen in Figure 9, where the amount of alkalinity in the effluent ALD water is plotted as a function of the time the water is in contact with the limestone (detention time). These data were obtained at four sites where sampling wells had been installed at regular intervals along the length of the ALD. The mine water increases in alkalinity as it travels through the ALD, until it approaches a maximum after about 15 to 20 hours of contact. As the shape of the plots in Figure 9 show, the ultimate level of alkalinity addition varies by ALD, but the rates at which the alkalinity level increases appear to be nearly first order with a half-life of about 5 hours. A minimum contact time of 15 hours ensures that at least 85 percent of the maximum achievable alkalinity is realized in the ALD.

The variation in the level of alkalinity addition cannot be attributed to the size of the limestone because it was the same for all four ALDs. There is a trend of increasing limestone dissolution with decreasing pH for the data presented; however, the final concentration of alkalinity produced in an ALD depends on factors other than just the pH of the water to be treated. An empirical test has been developed to estimate the alkalinity concentration that will be produced in an ALD using the actual mine water and limestone in collapsible containers (cubitainers) (Watzlaf and Hedin 1993). With this, we can determine limestone consumption rates, the quantity of limestone needed for a desired design life, and whether the ALD will make the mine water net alkaline.

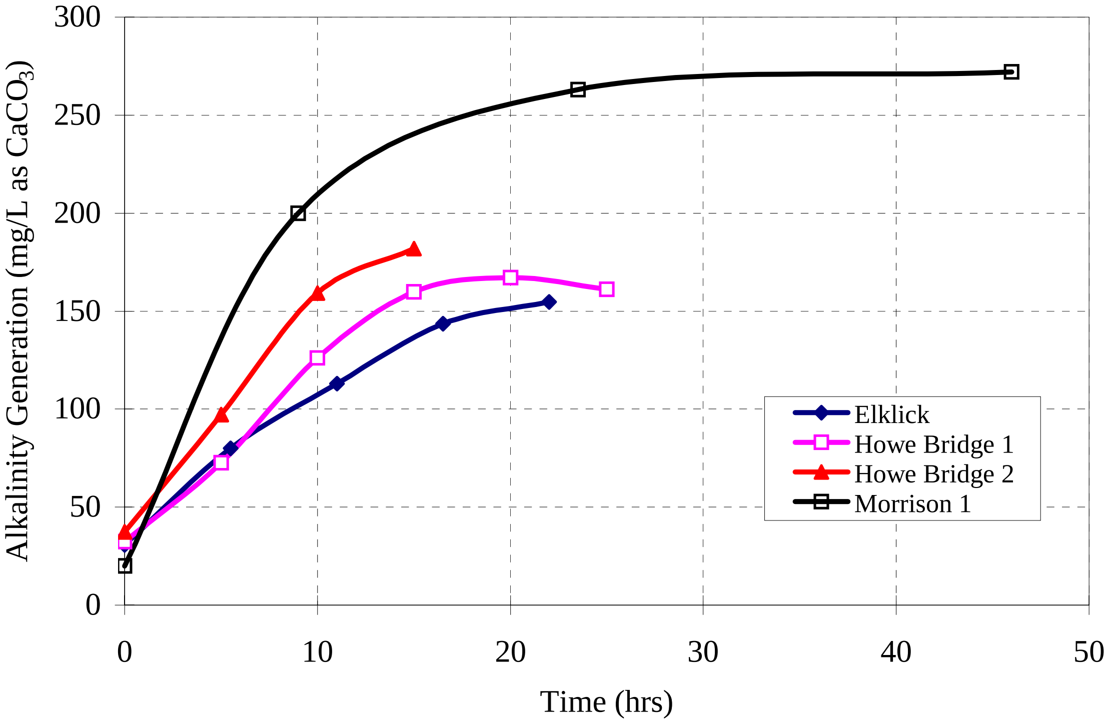

Figure 9. Alkalinity Concentration as Mine Water Flows through Selected ALD

All of the ALDs successfully add alkalinity, increasing the effluent levels by 50 to 270 mg/L. (See Table 11.) The smallest increases, observed at REM-R and REM-L, are undoubtedly the result of short detention times (7 to 8 hours) afforded by these ALDs. (See Table 10.) At half of the sites, a single ALD was sufficient to convert net acidic to net alkaline drainage. In the other five cases, the acidity produced from iron concentrations in excess of 200 mg/L was greater than the amount of alkalinity generated in the ALD. The increases in the alkalinity measured between the inlet and outlet of each drain correlate with the increase in calcium concentration. The average molar ratio of the increases in calcium and alkalinity, as $CaCO_3$, ((calcium out-calcium in)/(alkalinity out-alkalinity in)) was 1.02 for the seven cases for which all the data were available. This compares well with the expected ratio of 1.00. In general, ALDs receiving water low in aluminum and ferric iron concentrations, that have been designed with detention times greater than 15 hours have generated alkalinity at a consistent rate throughout their existence. (See Figure 10.) The effluent concentrations of alkalinity in the ALDs indicate consistent performance over the past ten years. The significantly higher alkalinity values for the last sample points for Filson R and L in Figure 10 were caused by very high detention times reflecting very low flows caused by the drought of 1999, which affected the entire state of Pennsylvania during that summer and into the fall. Detention times in these ALDs were increased by more than a factor of four during this low flow period. Flows at the other ALDs (Howe Bridge 1 and Elklick) shown in Figure 10 were not significantly affected by the drought. It is also of interest to note that no seasonal variation was observed for these ALDs, presumably because of the fairly narrow range of influent water temperatures, typical of groundwater, and relatively consistent flow rates.

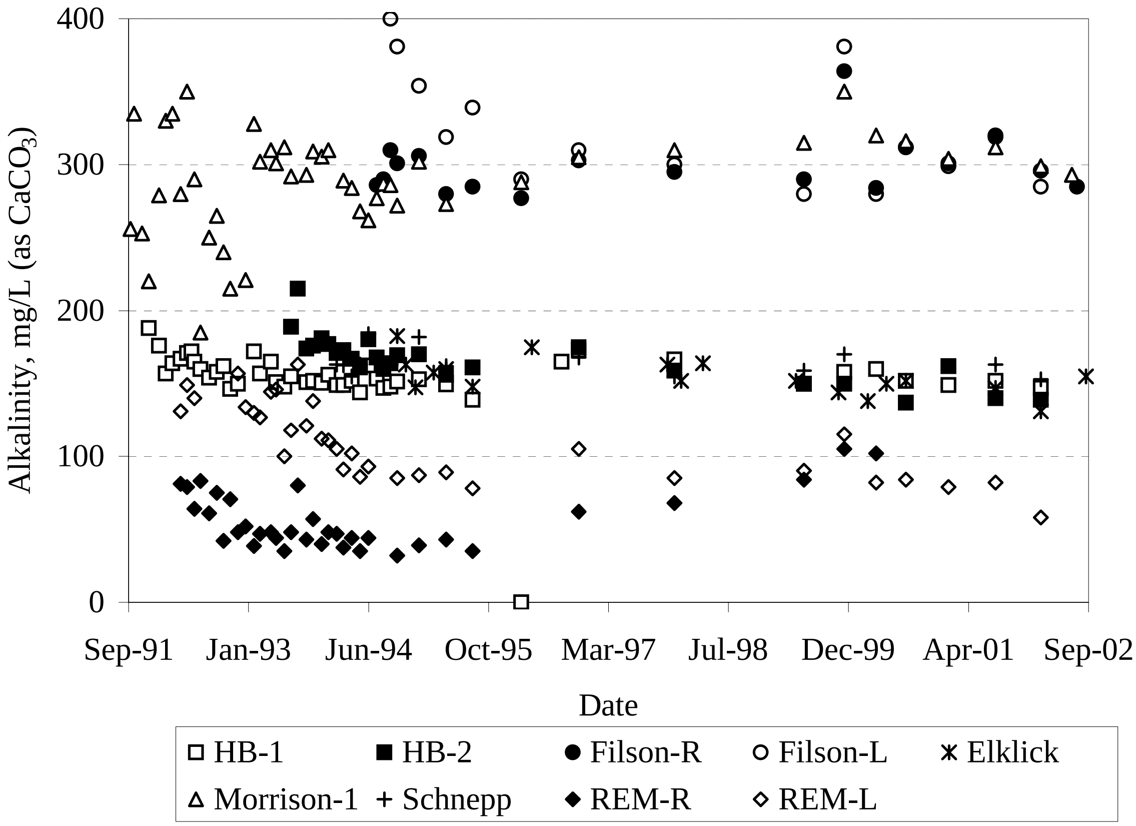

Figure 10. Effluent Alkalinity Concentrations of Selected ALDs Over Time

The amount of calcium carbonate remaining in these ALDs was calculated using the difference between the influent and effluent net acidity loadings over the period of time the system has been in use. Based on the quantity of limestone remaining, and assuming that the volume of the drain collapses around the shrinking core of limestone (i.e., void volume remains at 49 percent), the current detention times were calculated. As would be expected, detention times become shorter as the limestone is consumed. However, most ALDs are still operating at near maximum efficiency because detention times remain in excess of 15 hours. As an estimate of expected longevity, when the ALD detention time is expected to fall to the 15-hour minimum, the year was calculated from a linear extrapolation of the average rate of limestone consumption to date (last column of Table 9). Over half of the ALDs are still expected to meet or exceed their design life of 30 years. Resource constraints at the site resulted in the undersized construction of three ALDs. The Jennings ALD is no longer in operation because of clogging failure, and is described in more detail below.

Water Quality Changes

In addition to increases in calcium and alkalinity, changes in other effluent water quality parameters (pH, sulfate, and metals) were observed. Influent and effluent water quality analyses for the ALDs are presented in Table 11 and Table 12. At four of the ALDs (Howe Bridge 1, Howe Bridge 2, Elklick, and Jennings), influent samples could be collected immediately before the water flowed into the ALD. At three of the ALDs (Morrison, Filson-R, and Filson-L), seeps in the immediate vicinity were sampled to represent influent water quality. The remaining three ALDs (REM-R, REM-L, and Schnepp), based influent water quality on historical data.

Table 10. Initial and Current Conditions of ALDs

ALD Site	Year Built	Initial Conditions		Avg. Flow	Current Conditions		Year when t_d = 15 hours
		Limestone tonnes	t_d[1] hrs	L/min	Limestone tonnes	t_d[1] hrs	
Howe Bridge 1	1991	455	27	90.1	392	23	2024
Howe Bridge 2	1993	132	14	49.2	103	11	1993
Elklick	1994	165	25	35.8	147	22	2021
Jennings	1993	365	2	73.4	356	n/a	n/a
Morrison	1990	65	45	7.8	53	37	2035
Filson-R	1994	590	81	39.0	549	76	2100
Filson-L	1994	635	84	40.3	588	78	2086
Schnepp	1993	130	39	18.0	116	35	2047
REM-R	1992	125	6.0	112	92	4.4	n/a
REM-L	1992	125	7.1	94.5	75	4.3	n/a

The term t_d represents detention time. [1] *t_d based on limestone volume (V) and average flow (Q) using $t_d = V/Q$, assuming 49% porosity. n/a - not applicable*

Table 11. Average Water Quality Before and After Contact with the Anoxic Limestone Drain

ALD	Net Acidity,[1] mg/L as $CaCO_3$		Alkalinity, mg/L as $CaCO_3$		Calcium, mg/L		pH, s.u.		Sulfate mg/L	
	In	Out	In	Out	In	Out	In	Out	In	Out
Howe Bridge 1	461	344	33.2	155	154	206	5.72	6.29	1294	1294
Howe Bridge 2	396	265	37.3	161	148	201	5.44	6.45	1171	1175
Elklick	54.1	-59.2	35.2	155	79.4	130	6.01	6.65	338	333
Jennings	280	-33.5	0	139	ND	201	3.23	6.16	633	620
Morrison[2]	382	55.3	28.4	280	113	222	5.18	6.33	1246	1039
Filson-R[2]	57.2	-154	48.1	300	69.6	186	5.61	6.41	411	427
Filson-L[2]	57.2	-168	48.1	323	69.6	175	5.61	6.52	411	401
Schnepp[3]	307	-22.7	0	165	69.2	199	3.28	6.16	980	768
REM-R[3]	1148	819	0	56	258	228	4.28	5.41	2825	2338
REM-L[3]	ND	256	ND	110	ND	202	ND	5.94	ND	1225

[1] *Negative net acidity values indicate net alkalinity.* [2] *"In" concentrations based on water quality of a nearby seep.* [3] *"In" concentrations based on historical water quality data of the untreated mine drainage prior to construction of the ALD. Numbers are not available for REM-L. ND = Not Determined.*

Table 12. Additional Water Quality Parameters Before and After Contact with the Anoxic Limestone Drain

ALD	Iron, mg/L		Manganese, mg/L		Aluminum, mg/L		Cobalt, mg/L		Nickel, mg/L		Zinc, mg/L	
	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
Howe Bridge 1	270	268	41.1	40.8	<0.2	<0.2	0.44	0.44	0.49	0.48	0.58	0.51
Howe Bridge 2	223	239	35.0	34.8	<0.2	<0.2	0.37	0.37	0.38	0.38	0.41	0.36
Elklick	56.0	54.2	4.72	4.82	<0.2	<0.2	0.07	0.07	0.10	0.09	0.14	0.08
Jennings	75.6	59.3	8.39	8.33	20.9	1.1	0.13	0.15	0.40	0.40	0.66	0.54
Morrison[1]	208	157	48.3	40.4	0.6	<0.2	0.86	0.72	0.79	0.64	0.98	0.66
Filson-R[1]	57.6	51.6	20.8	19.1	0.4	<0.2	0.24	0.23	0.19	0.18	0.23	0.22
Filson-L[1]	57.6	68.1	20.8	16.9	0.4	<0.2	0.24	0.14	0.19	0.13	0.23	0.16
Schnepp[2]	92.0	66.2	28.0	27.4	6.7	<0.2	ND	0.29	ND	0.35	ND	0.36
REM-R[2]	589	437	136	123	4.5	3.2	ND	1.44	ND	1.46	ND	2.36
REM-L[2]	ND	180	ND	50.6	ND	<0.2	ND	0.59	ND	0.64	ND	0.72

[1] "In" concentrations based on water quality of a nearby seep. [2] "In" concentrations based on historical water quality data of the untreated mine drainage prior to construction of the ALD. ND - Not Determined

In general, the pH increased as the alkalinity increased, until a pH of about 6.4 was achieved above 160 mg/L. The seven pH measurements corresponding to alkalinities above 150 mg/L gave an average pH of 6.45 ± 0.20 s.u. Thus, the effluent of an ALD resembles a bicarbonate buffered solution, as would be expected for a mixture of mineral acid and carbonate alkalinity.

Sulfate concentrations were not affected by the ALDs. The first 4 entries in Table 10, which represent matched influent/effluent samples, never show more than a 15 mg/L loss of sulfate. Subsequent entries do show some larger sulfate loses, but only historical or adjacent seep data are available for the influents, making the apparent losses suspect, since sulfate losses would not be expected in these ALDs. Chemical precipitation as gypsum is unlikely at these concentrations. These ALDs do not contain added organic matter, which acts as ion exchange material, or a source of carbon for sulfate-reducing anaerobes, such as occurs in RAPS. Although sulfate reduction does not appear to be active in the systems studied here, it cannot be ruled out for all ALDs. In some cases, mine drainage becomes associated with other pollution sources, such as feed lot runoff or contributions from leaking sewers or septic systems. In such cases, a source of organic carbon would be present, which could provide an acceptable environment for anaerobic, sulfate-reducing bacteria within the ALD.

In those cases where matched influent and effluent samples were obtainable (Howe Bridge 1, Howe Bridge 2, Elklick, and Jennings), the iron balances (with the exception of Jennings) indicated iron was not retained within the ALD. The influent water at Jennings contained both ferrous and ferric iron. At the other three sites, all of the iron was in the ferrous form (>99 percent). As already discussed, at the sites where inlet concentrations were estimated from historical data, the listed "in" value probably overestimated the contamination actually entering these ALDs. Manganese balances across the ALDs indicated little or no retention. Chemical precipitation as an oxide or hydroxide would not be expected in water having a pH of less than 7 under anoxic conditions. Although manganese carbonate precipitation is a possibility, there was no indication of this at the ALDs in this study.

Only water at three of the sites water contained aluminum in excess of 1 mg/L. The highest aluminum concentration was observed at the Jennings site (21 mg/L) and is most probably the reason for the premature failure of this ALD. The REM-R and Schnepp ALDs received 4.5 and 6.7 mg/L of aluminum (based on historical water quality). The REM-R ALD recently failed after 10 years of treatment, with no water emanating from the effluent pipe. All of the water is bypassing the ALD, presumably the result of a significant reduction in permeability. The Schnepp ALD has continued to operate since 1993. Because the actual influent water samples were unobtainable, the average aluminum concentrations at these two ALDs is uncertain, but is presumed at somewhat less than the original 5 to 7 mg/L. The untreated mine water quality at other sites in this watershed has shown a general and significant improvement over the past ten years. Therefore, using historical data for the influent water quality may bias the data toward the more contaminated water samples analyzed 10 or more years ago.

The concentrations of cobalt, nickel, and zinc were low in these waters and seldom exceeded 1.0 mg/L. Cobalt and nickel do not appear to be retained in the ALDs. The appearance of Zinc diminishes in all of the effluents, but only by 0.1 mg/L or less. Some removal of zinc at higher concentrations (ca. 5 to 10 mg/L) in ALDs has been reported by Nuttall and Younger (2000).

Premature Failure of Two ALDs

Jennings

Construction of the ALD at the Jennings site was completed during April 1993. Although the ALD successfully reduced the acidity of the mine water, the amount of flow passing through it began to decrease after 4 to 5 months, as a small leak developed near the beginning of the third ALD cell. The flow from this leak progressively increased until it accounted for more than 80 percent of the total flow after 9 months of operation.

Analysis of the water quality and flow data provided insight into the possible mechanisms of failure. Essentially 100 percent of the aluminum was retained within the ALD. Most of the ferric iron, which accounted for about 10 percent of the total iron in the mine water, was also retained in the ALD. Nearly 100 percent of these two species were retained with no loss in efficiency, even as the flow deceased towards the end of 1993. Both of these species form stable precipitates under the ambient conditions in the ALD, and are undoubtedly responsible for the decreasing permeability and eventual clogging of the drain. In addition to the constant removal of the two easily precipitated species, there is an initial retention of ferrous iron during the first few months of operation, probably due to oxygen scavenging by the ferrous species, adsorption on limestone surfaces or ion exchange on clay minerals in the limestone. During construction, the air in the drain contains oxygen, which is available for reaction if it is not flushed from the system prior to operation. Up to 40 percent of the iron retained in the drain may have resulted from the oxidation of ferrous iron and the subsequent precipitation of ferric hydroxide.

The total quantity of retained material was calculated at 581 kg of aluminum and 572 kg of iron. Thus, a combination of both iron and aluminum could be responsible for clogging the Jennings ALD. However, it might be argued that aluminum was more important for two reasons.

First, given the assumption that about 40 percent of the iron precipitate was caused by oxidation, and some of the remainder by adsorption processes, it probably occurred throughout the ALD, rather than in the one section, where the actual plug developed. Second, the portion of the ALD where the clog was suspected was excavated, revealing the formation of a white gelatinous substance, similar to aluminum precipitates seen elsewhere. Aluminum is thought to be the major cause of failure at this site. In the absence of reducing conditions, such as those generated in RAPS, the ferric iron in the influent may have also contributed to the problem.

REM

Construction of the REM ALD was completed in 1992. The ALD produced an average of 54 mg/L of alkalinity with its 6.8 hours of detention time. About 6 years after construction, water was noted leaking from the ALD. Effluent flow was significantly reduced after 9 years of operation, and the volume of leakage increased. In year 10, the effluent stopped flowing completely.

Only historical influent water quality exists for this site. Prior to construction of the ALD, the mine discharge contained 4.5 mg/L of aluminum. Throughout the 10 years of monitoring this ALD, aluminum floc was observed emanating from the effluent pipe. If the effluent pipe was blocked (by hand) for 30 to 60 seconds, a slug of aluminum precipitates would flow out of the effluent pipe. This indicates that aluminum solids were precipitating within the ALD and were most probably the cause of its eventual failure.

Compost Wetlands

Mine water containing Fe^{3+}, aluminium, or dissolved oxygen (DO) concentrations greater than 1 mg/L has been treated with surface-flow compost wetlands. Compost wetlands generate alkalinity through a combination of bacterial activity and limestone dissolution. The desired sulfate-reducing bacteria requires a rich organic substrate which allow anoxic conditions to develop. Limestone dissolution also occurs readily within this anoxic environment. A substance commonly used in these wetlands is spent mushroom compost, a substrate that is readily available in western Pennsylvania. However, any well-composted equivalent should serve as a good bacterial substrate. Spent mushroom compost has a high $CaCO_3$ content (about 10 percent dry weight), but mixing in more limestone may increase the alkalinity generated by $CaCO_3$ dissolution. Compost substrates that do not have a high $CaCO_3$ content should be supplemented with limestone. The compost depth used in most wetlands is 30 to 45 cm. Typically, a ton of compost will cover about 3.5 square yards about 45 cm thick. Cattails or other emergent vegetation are planted in the substrate to stabilize it, and to provide additional organic matter to “fuel” the sulfate reduction process. As a practical tip, cattail plant/rhizomes should be planted deep into the substrate prior to flooding the wetland cell.

Compost wetlands, in which much or most of the water flows over the surface of the compost, remove acidity (e.g., generate alkalinity) at rates of approximately 2 to 12 $g\ d^{-1}\ m^{-2}$. This range in performance is largely a result of seasonal variation: acidity removal rates are lower in winter than in summer (Hedin et al., 1991). Hedin et al. (1994a) recommended sizing compost wetlands based on acidity removal rates of 3.5 to 7 $g\ d^{-1}\ m^{-2}$. Since the beneficial reactions occur in the compost and limestone layers, and not in the surficially flowing water, these systems must be quite large. For the past 5 years or so, reducing and alkalinity-producing systems (RAPS) have been used to treat net acidic water containing ferric iron, aluminum, or DO concentrations greater than 1 mg/L, instead of compost wetlands. However, at sites with sufficient land area and/or minimal elevation difference between the mine discharge and the stream, compost wetlands may be the most appropriate choice.

Reducing and Alkalinity-Producing Systems (RAPS)

RAPS is a generic term that describes the chemistry within a certain type of passive treatment. In addition to producing alkalinity via dissolving limestone, these systems promote reducing conditions by incorporating organic matter. The RAPS design directs water to flow down through organic matter into the limestone. The reducing conditions facilitate sulfate reduction, which generates alkalinity (reaction Y), and may also precipitate some metals to sulfides. Ferric iron can be reduced to ferrous iron, eliminating the precipitation of ferric hydroxide and subsequent clogging and armoring of the limestone.

$$2\ CH_2O = SO_4^{2-} \rightarrow H_2S + 2\ HCO_3^- \qquad (Y)$$

This type of system was first implemented by Doug Kepler at the Howe Bridge site. These systems were termed successive alkalinity-producing systems (SAPS), indicating that more than one of these units could be used in series to treat very highly acidic water (Kepler and McCleary 1994). Similar systems have also been referred to as vertical flow systems, vertical flow ponds, or vertical flow wetlands. Chemically, biologically, and physically these systems behave similarly, and will be referred to as RAPS in this manual. A layer of limestone (0.6 to 1.2 m thick) is placed on the bottom of an excavated area. A network of perforated pipes is placed in the lower portion of this limestone layer. Organic material (0.15 to 0.61 m thick), which typically has been composted, is placed above the limestone, and serves as the nutrient source for the sulfate reducing bacteria. In Pennsylvania, spent mushroom compost has been the organic material of choice. It roughly consists of composted horse manure (56 percent by weight), hay (22 percent), straw (10 percent), chicken manure (10 percent), and gypsum (2 percent), but can differ between mushroom farms, since each uses its own recipe. Mine water flows down through the system, encountering reducing conditions within the compost before contacting the limestone. In the reducing environment, dissolved oxygen is removed, which prevents ferrous iron oxidation, and any ferric iron already present is reduced to the ferrous state. Thus, RAPS are appropriate for water containing ferric iron, which could armor the limestone in an ALD.

It is thought that RAPS may also be more resistant to plugging by aluminum than ALDs because of their larger cross sectional area and higher available head pressures (Watzlaf and Hyman 1995). The oldest RAPS in this study (Howe Bridge) treated water for 11 years before being replaced. After 11 years, it was still able to pass 50 percent of the influent water through the compost and limestone layers. This system received less that 0.2 mg/L of aluminum. It appeared that the progressive reduction in permeability was due to precipitation of iron hydroxides on top of the compost layer, with an accumulation of iron sludge in excess of 15 cm on top of the compost. Reduced permeability may also result from storm-mobilized silt and other solids, as well as precipitation of metal sulfides within the organic layer. Thus, continued monitoring of the actual performance of these systems is warranted.

In practice, RAPS, ALDs, settling ponds, and aerobic wetlands are used as unit operations in a total remediation system. For example, RAPS are usually preceded by a settling pond/wetland to settle iron and other solids, which could reduce permeability of the system. RAPS and ALDs are followed by settling ponds and aerobic wetlands for oxidation, precipitation, and settling of metals. After these ponds and wetlands, additional RAPS may be used, each separated by a settling pond and wetland, to sequentially improve the water quality when sufficient alkalinity cannot be introduced in the initial ALD or RAPS.

Site Descriptions

Howe Bridge - Water flows through a compost wetland (0.14 ha) prior to entering a RAPS (0.14 ha). The RAPS contains a 0.4-m layer of limestone gravel covered by a 0.2-m layer of spent mushroom compost and about 1.5 m depth of water. Perforated drainage pipes (black plastic corrugated sewer pipe) are placed in a serpentine pattern in the bottom of the limestone layer. These pipes only cover about one-half of the total surface area of the system (~0.07 ha). Influent water is collected prior to the compost wetland.

Oven Run D (#1 and #2) - This system treats discharges from reclaimed surface and daylighted deep mines. Two RAPS are in series, each with a surface area of about 0.15 ha. Both contain a 0.91-m thick layer of limestone and a 0.15-m thick layer of compost covered by 1.5 m of water. a wetland precedes each RAPS with a surface area of 0.11 ha and a depth of 0.076 to 0.152 m of water. Influent water for each RAPS is sampled prior to the wetlands.

Oven Run E (#1 and #2) - Abandoned deep mine drainage is piped to two RAPS in a series. Each RAPS has a surface area of 0.26 ha, and the same thickness of limestone, compost and water as the Over Run D RAPS, outlined above. RAPS #1 is preceded by a 1.8-m deep pond (0.10 ha) and a wetland (0.12 ha). RAPS #2 is preceded by a pond (0.11 ha) and a wetland (0.11 ha).

Jennings - A system of perforated pipes was placed within a 0.31-m thick bed of inert river gravel, which was wrapped with a geotextile fabric. Above the gravel layer is a mixture of limestone and spent mushroom compost that is 0.8 m thick. This mixture consists of 270 tonnes of compost and 345 tonnes of limestone aggregate (9.5 mm x 1 mm (i.e., 3/8 in x 16 mesh)). Influent water is sampled prior to entering the RAPS (Jennings Water Quality Improvement Coalition 1999).

Results

While alkalinity is produced solely by limestone dissolution in ALDs, it is produced by both limestone dissolution and sulfate reduction in RAPS. Table 13 and Table 14 present the data obtained for six RAPS that have been monitored for up to 9 years. Shown in Table 13 are: (1) the alkalinity produced by limestone dissolution (based on increases in calcium, where a 1 mg/L increase stoichiometrically yields 2.497 mg/L of alkalinity as $CaCO_3$); (2) the alkalinity produced by sulfate reduction (based on decreases in sulfate, where a 1 mg/L decrease stoichiometrically yields 1.042 mg/L of alkalinity as $CaCO_3$); (3) the measured total alkalinity generated by the RAPS; and (4) the specific rate of generation of alkalinity calculated as grams per day, per square meter of surface area, measured at the top of the compost layer.

Table 13. Construction Specifications and Quantification of Alkalinity Generation within RAPS

RAPS Site	Howe Bridge	Oven Run D #1	Oven Run D #2	Oven Run E #1	Oven Run E #2	Jennings
Yr Built	1991	1995	1995	1997	1997	1997
Avg. Flow, L/min	70.9	342	323	408	413	61.4
Compost						
Qty, tonnes or m3	272 t	140 m^3	140 m^3	248 m^3	248 m^3	270 t
td1, hr	8.8	1.7	1.8	2.5	2.5	24
Alkalinity by SO_4 reduction mg/L as $CaCO_3$	92	25	41	61	21	57
Limestone						
Qty, tonnes	454	1349	1349	2425	2425	345
Td1, hr	34	21	22	32	32	24
Alkalinity by limestone dissolution, mg/L as CaCO3	120	70	4	130	30	419
Total Measured Alkalinity Generated 3, mg/L as CaCO3	212	97	29	149	58	424
Alkalinity Generation Rate, $gd^{-1}m^{-2}$	18.2 - 36.3	53.5	17.1	40.3	16.2	60.4

[1] *td based on quantity of limestone or compost at construction and average flow rates using td = V/Q and assuming void volumes of 49 percent for limestone and specific yields of 25 percent and 20 percent for compost and compost/limestone mixture, respectively.* [2]*Jennings contained a compost and limestone mixture, the 25-hr td is for the mixed layer.* [3]*Total alkalinity generated based on changes in measured net acidity between the influent and effluent of RAPS.*

The Howe Bridge RAPS produced approximately equal amounts of alkalinity from sulfate reduction and limestone dissolution over the past 9 years. Much of the alkalinity that was derived from sulfate reduction occurred in the first 2 to 3 summers of operation. (See Figure 11.). Seasonal trends in sulfate reduction were shown in the first few years of operation. Although it is more difficult to see seasonal trends in more recent years because of lower sampling frequency, it is apparent that the alkalinity production is not reaching the high levels achieved in the first few years. Alkalinity generation rates were calculated as 19.6 g d^{-1} m^{-2} using the total surface area of the top of the compost. However, the perforated piping in the limestone layer extended only about half way into the system, potentially causing it to perform as if water actively flowed through only half of the RAPS. Taking this into account, actual alkalinity generation rates are probably on the order of 39 g d^{-1} m^{-2}.

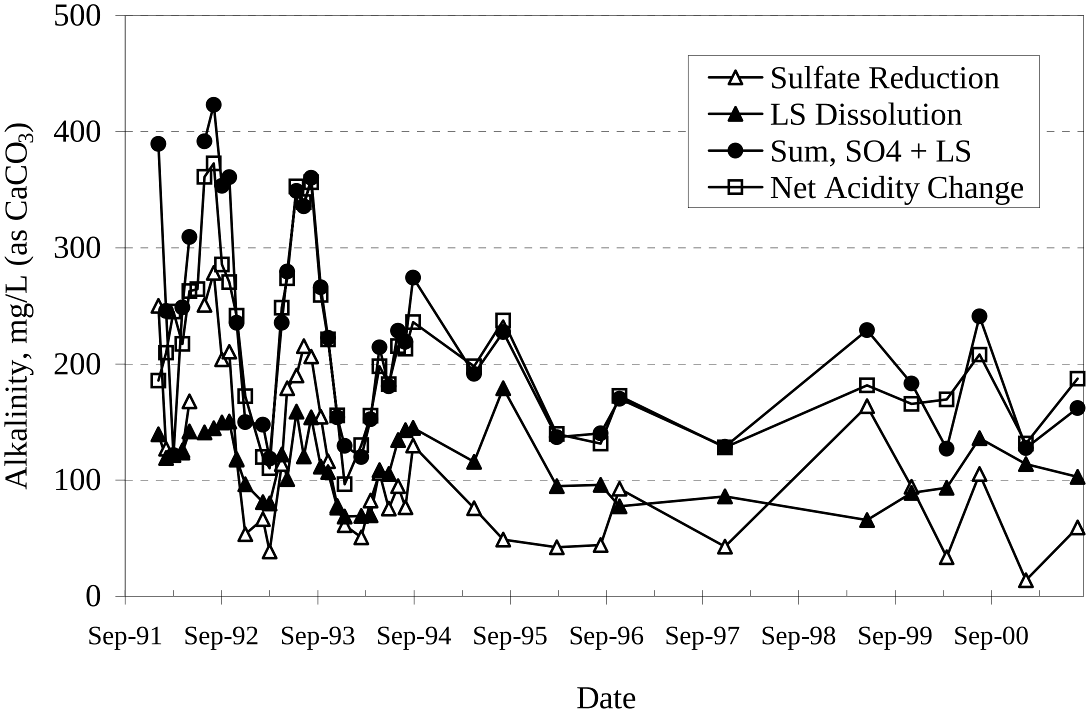

Figure 11. Alkalinity Generation in the Howe Bridge RAPS

Alkalinity from sulfate reduction and limestone (LS) dissolution were calculated from differences in sulfate and calcium, respectively. The sum of these calculated alkalinities is also plotted with actual measured changes in net acidity.

Both Oven Run sites consist of two RAPS in series. The rationale for this was twofold: (1) one system could be put offline for maintenance and (2) during the design life of the two RAPS, the first system was expected to contribute more alkalinity during the first half, and the second system would contribute more alkalinity in the last half. At site D, the first RAPS produced alkalinity at a rate of 57.4 $gd^{-1}m^{-2}$, and the second at a rate of 20.6 $gd^{-1}m^{-2}$ over five years of operation. Similarly, at site E, the first RAPS produced alkalinity at a rate of 42.7 $gd^{-1}m^{-2}$, and the second at a rate of 15.6 $gd^{-1}m^{-2}$, over three years of operation. It was difficult to determine any seasonal trends in the alkalinity production at either site because of the low sampling density and extremely variable flow rates at each site (a very wet period, followed by an extended drought period produced a greater than tenfold difference between high and low flows).

For the Jennings RAPS, the compost and limestone were mixed together instead of maintaining two distinct layers. This design was chosen because laboratory tests indicated that the water at Jennings was capable of depleting the calcium carbonate within a 0.7-meter thick layer of spent mushroom compost in about two years (Watzlaf 1997). After the calcium carbonate was depleted in the laboratory tests, sulfate reduction virtually ceased, presumably because of the lower pH environment. At this lower pH, fermentative bacteria, as well as sulfate-reducing bacteria may not be as active. The fermentative bacteria breaks down complex organics into simpler forms that the sulfate reducers can use. The rapid depletion of calcium carbonate was caused by the production of acidity during aluminum precipitation (an aluminum concentration of 23 mg/L will produce 128 mg/L of acidity upon hydrolysis). The Jennings RAPS produced the greatest change in net acidity of any of the systems, attributing over 90 percent of the alkalinity production to limestone dissolution. As discussed above, some (128 mg/L) of this change can be attributed to aluminum precipitation. This RAPS displayed no clear seasonal trends.

Table 14 shows changes in the major water quality parameters. The change in calcium and sulfate concentrations were used to estimate the contributions of limestone dissolution and sulfate reduction, respectively, as described above. Net acidity was determined using the peroxide oxidation method, and the change in net acidity between the inlet and outlet is listed as the total alkalinity generated in the second to last column in Table 13. Manganese, which is expected to be conserved in these systems, was present in the influent and effluent at about the same levels. Iron, and aluminum when present, were retained by the systems.

Table 14. Water Quality Before and After Contact with Reducing and Alkalinity Producing System

RAPS		Howe Bridge	Oven Run D #1	Oven Run D #2	Oven Run E #1	Oven Run E #2	Jennings
Net Acidity, mg/L as CaCO3	**In**	314	99.8	6.38	212.	63.2	272
	Out	102	2.56	-23.0	63.2	5.3	-152
Alkalinity, mg/L as $CaCO_3$	**In**	31.3	1.5	N/A	0.0	9.4	0.0
	Out	57.8	29.0	31.6	9.4	25.5	204
Calcium, mg/L	**In**	190	300	327	149	201	109
	Out	238	328	328	201	213	277
Iron, mg/L	**In**	189	40.6	1.69	18.6	9.21	68.5
	Out	72.1	3.41	0.47	9.21	3.93	14.7
Manganese, mg/L	**In**	37.0	28.2	27.3	12.1	11.9	18.6
	Out	35.7	27.4	22.0	11.9	11.3	17.6
Aluminum, mg/L	**In**	<0.2	1.45	1.21	16.4	9.40	24.1
	Out	<0.2	0.82	0.32	9.40	4.36	0.84
Sulfate, mg/L	**In**	1186	1356	1340	932	873	799
	Out	1098	1332	1301	873	853	744

The majority of these metals were presumably retained in the wetlands that precede the RAPS, though significant levels of iron may have been removed on top of the compost in the RAPS. However, the Jennings site has no such wetland and retains 85 percent of the iron and all of the aluminum. In some cases, such as the Oven Run E sites, preventative maintenance is performed by periodic high-flow flushing, during which the RAPS pond level is lowered. The results of two flushes are reported below. Additional details of these and other flushes can be found in Watzlaf et al. (2002).

Case Study: Flushing the DeSale II RAPS

The DeSale II site is located in Butler County, Pennsylvania within the headwaters of Seaton Creek, a heavily impacted tributary in the Slippery Rock Creek Watershed. The system consists of an equalization pond, two RAPS, an oxidation pond, wetlands, and a horizontal limestone bed. Each RAPS is approximately 100 m long and 16 m wide and consists of (from the bottom up) 15 cm of limestone for pipe bedding (AASHTO #57), the lower discharge/flush pipes, 60 cm of limestone (AASHTO #1 is approximately 10 cm, 90 percent calcium carbonate), the upper discharge/flush pipes, 60 cm of limestone (AASHTO #1), 15 cm of spent mushroom compost, and 75 to 90 cm of water. Networks of piping drain four quadrants at two different vertical levels (upper and lower) within the system. This more extensive underdrain system was developed in an attempt to optimize both the distribution of flow during normal operation, and the flushing of accumulated iron and aluminum solids. The underdrain was constructed of 10-cm diameter Schedule 40 PVC pipe. Perforated laterals were placed on 1.4-m centers and connected to an unperforated header with a sanitary-type tee. Perforations were hand-drilled with two, 1.3-cm perforations, which were offset approximately 30 ^{o} from the top of pipe. The perforation spacing was equal to the lateral spacing (1.4 m). Four separate header pipes were used for each underdrain level, thus dividing the surface area into approximately equal quadrants. The upper and lower underdrain levels effectively divide each RAPS into eight separate cells, four upper and four lower.

In the two years after its completion, the RAPS functioned very effectively, increasing pH from 3.1 to 6.9, adding 370 gm/L of alkalinity, and decreasing iron and aluminum concentrations from 27 to 5 mg/L, and 11 to 0.3 mg/L, respectively.

The right system was flushed nine months after it began treating water. Each of the eight pipes was flushed sequentially at full volume (660 to 1360 L/min per pipe) for nine minutes. A total of 69,700 L of water was removed (~ 4 percent of the total volume of water in the RAPS). Samples were collected at 15, 30, and 45 seconds, then at 30 second intervals from 1 to 5 minutes, and then at 1-minute intervals from 5 to minutes. Dissolved oxygen, temperature, and pH were monitored continuously and recorded at each sample interval. Flows were measured periodically (~ every 1 to 3 minutes) using three different methods: horizontal pipe discharge method, time volumetric method, and water level changes in RAPS. All three flow measurement techniques were in fairly good agreement (within ~ 15 percent). Samples were not filtered and consisted of an unacidified and acidified sample. Samples were analyzed in the laboratory for concentrations of standard and trace mine drainage metals and sulfate.

The left system was flushed after 14 months of treatment. Based on the results of the first flush, it was decided to flush the left system much more aggressively (i.e., to drain the system completely). The pipes draining the four upper quadrants were opened at the same time. After these pipes had drained for 11 hours, the flow had diminished to a trickle. After closing the valves to the upper pipes, the lower flush pipes were opened and drained for an additional 4.5 hours. Flows were measured periodically (every 10 to 20 minutes) using the horizontal pipe discharge method, which had compared favorably to the timed volumetric method and water level changes method during the previous flush. A total of 1,430,000 L of water was removed from the system. Unfiltered samples were collected from each pipe at 10 minute intervals. Temperature, pH and flow measurements were taken between sample collection.

The two RAPS at the De Sale II site are essentially equivalent. They were constructed in parallel, have the same dimensions, contain the same type and amount of media (limestone, compost, etc.) and receive water from a common source.

From available monitoring data, including flow measurements and water quality analyses, it was calculated that the right RAPS had accumulated 780 kg of iron and 312 kg of aluminum during the first nine months of operation. The basic criterion used during this flush was that the water should be allowed to flow until it ran clear. In practice, the flush was actually continued for some additional time. During the flush, a total of 69,700 L of water was removed. The maximum metal concentrations occurred in the first few minutes of flushing when the water was visibly discolored. Both the visual observations and the lab analyses indicate that the initial slug of material was removed from the system within two minutes. After seven minutes of flushing, the iron and aluminum concentrations were the same as the concentration of dissolved metal, indicating that no solid material was eluting.

Integration of the concentration versus time graphs indicated that only 1.4 kg of iron (0.2 percent of the iron retained since construction) and 0.9 kg of aluminum (0.3 percent of the aluminum retained since construction) were flushed from the system. If one assumes that the water flowed into the pipe uniformly from every direction, the range of influence of this flush can be estimated from the pipe dimensions, the gallons flushed, and by assuming a limestone porosity of about 50 percent (Hedin and Watzlaf 1994). It is estimated that the last water through each pipe had been, on average, only 10 cm from the pipe before the flush began. Thus, it is doubtful that much, if any of the metal oxyhydroxide-laden water actually entered the pipes during this limited flush. Our conclusion is that “flushing until the water runs clear” is probably not a sufficient criterion for effective flushing.

The left RAPS was flushed 14 months after it began treating water. From available monitoring data, including flow measurements and water quality analyses, it was calculated that the RAPS had accumulated 948 kg of iron and 499 kg of aluminum during these first 14 months of operation. Because of the low amount of metals removed during the flushing of the right RAPS, the criterion used during this flush was that the water should be allowed to flow as long as possible (i.e., until the system was drained). In practice, the four pipes draining the upper quadrants were flushed until the flow slowed to a trickle, then the pipes draining the lower four quadrants were opened and allowed to flow until the system was totally drained. During the flush, a total of 1,430,000 L of water was removed. To a first approximation, the flows in both the upper and lower sections decrease going from quadrant 4 to quadrant 1. Qualitatively, this is consistent with the pressure drop expected because of the increasing length of 10 cm diameter pipe draining the quadrants. However, it would also be consistent with a clogging mechanism in which the settling of suspended material, such as clays, predominated in the quadrants closest to the RAPS inlet. The flows dropped slowly at first, and then more rapidly after the first 7 to 8 hours. At about 11 hours, the upper quadrants had drained and the valves to the lower quadrants were opened. Flows were higher and longer for the upper quadrants than for the lower quadrants,because these pipes drained, the standing water, the compost water, and the top limestone layer (total of 1.5 m of head), whereas the lower quadrant pipes drained only the bottom limestone layer (0.6 m of head).

The temperature and pH were monitored throughout the flush. The trends for both parameters were the same; both decreased as the cooler, more acidic surface water penetrated the lower strata faster than the chemical and thermal equilibration could occur. At about 7 hours the values began to climb toward their earlier levels. This was at the same point at which the flow sharply decreased (and residence time increased) indicating that the thermal and chemical equilibration rates were now becoming competitive with the flow rate. At a little over 8 hours (where the breaks in the upper quadrant trend lines occur), it was necessary to shut off the flow due to darkness. The next morning, the temperature and pH continued to increase further to near their initial values. The pH actually attained somewhat higher values, perhaps because of the overnight stoppage of flow during which extended contact with the limestone occurred.

The maximum metal concentrations occurred in the first few minutes and corresponded to visibly discolored water similar to what was seen for the right RAPS flush. In total, little additional material was removed from the system even after prolonged flushing. Of the retained

948 kg of iron and 335 kg of aluminum, the flush removed 10.0 kg of iron (1.1 percent of the iron retained since construction) and 6.53 kg of aluminum (1.3 percent of the aluminum retained since construction).

Prior to the flush, no decrease in the permeability of the RAPS had been observed. Using a hand level, there was no measurable (< 1.5 cm) difference in the elevation between the RAPS water level and the level of the discharge pipe, indicating that very little head was necessary to push the water though the RAPS. The system was probably maintaining permeability because very little void volume had been lost up to that time. The 948 kg of retained iron corresponds to 1810 kg of $Fe(OH)_3$. Our measurements indicate that a cubic centimeter of iron sludge contains 0.17 g of iron. Using this value, approximately 5.58 m^3 of iron sludge was retained in the RAPS. Making similar assumptions for the aluminum sludge results in 2.92 m^3 of aluminum sludge, for a total sludge volume of 8.50 m^3. Assuming a 25 percent void in the compost and a 50 percent void in the limestone, the RAPS contains about 595 m^3 of void space, with the precipitated sludge occupying only about 1.4 percent of this void. Thus, it may be argued that too little material had accumulated to be flushed effectively. Larger masses of material would present a larger cross-sectionof the rapidly flowing water, more likely to be transported down-flow.

It is important to note that it is unlikely that the precipitates were distributed uniformly throughout the available void volume. It is more likely that precipitation occurred in a band (Watzlaf 1997). The width and position of the band would be determined by the pH gradient and rates of precipitation and agglomeration. Therefore, the permeability of the RAPS could be significantly reduced long before 100 percent of the void volume was occupied.

It is interesting to note that, although the clogging of RAPS is thought to be due to aluminum precipitation, iron is being retained as well. The amounts of iron and aluminum being retained in these systems are shown in Table 15.

Table 15. Total Amounts of Retained Iron and Aluminum Prior to Flushes at the DeSale II Site

RAPS	Fe Retained (kg)	Al Retained (kg)	Fe/Al Molar Ratio
Right	780	312	1.21
Left	948	499	0.92

Table 16. Amount of Water, Iron, and Aluminum Flushed for the Two RAPS at the DeSale II Site

RAPS	Water Flushed		Iron Flushed		Aluminum Flushed	
	L	% of total	kg	% of retained	kg	% of retained
Right	69,700	5	1.4	0.2	0.9	0.3
Left	1,430,000	100	10.0	1.1	6.5	1.3

Neither flush removed very much of the retained iron or aluminum. The most efficient flush achieved only 1.1 percent removal of the incremental amount of metals accumulated since the previous flush. (See Table 16.) None of the systems were experiencing any loss of permeability prior to the flushes. In fact, only a very small percentage (1.1 to 1.4 percent) of the void volumes were calculated to be filled with iron and aluminum precipitates. Lack of efficiency has not yet led to failures of these systems and, in one case, efficiency may be improving with time. However, the long-term prospects for these systems appear questionable at best, if the current levels of metal removal via flushing continue.

Other Types of Water Treatment Systems

There are several other types of systems treating coal mine drainage, ranging from purely passive, to semi-passive, to active. Table 17 lists many of these technologies with their electricity requirement, the presence of moving parts, the required frequency of minor and major maintenance, frequency of chemical addition, and estimated design life. Brief descriptions of some of the widely used systems are given below (including the systems already discussed in this paper). Further description and a listing of additional types of systems can be found elsewhere (USEPA 1983, Younger et al. 2002, Brown et al. 2002, EPA 1983, PIRAMID Consortium 2003).

Aerobic Wetlands — Effective for the treatment of net alkaline mine drainage, aerobic wetlands typically consist of an aeration structure (riprapped ditch, waterfall), a deep unvegetated pond (1.2 to 2.4 m deep) and a shallow wetland (~0.15 m deep) that usually contains cattails (typically *Typha latifolia*). The deeper ponds are designed to hold precipitated iron oxides, while the cattail wetland is used to remove remaining dissolved and suspended iron.

Anoxic Limestone Drains — Buried beds of limestone are designed to intercept mine water in an anoxic state and add bicarbonate alkalinity. The presence of aluminum and ferric iron will result in precipitation of these metal hydroxides within the ALD and could lead to premature failure by limiting the reactivity of limestone and/or clogging with these precipitates. Aerobic wetlands are used after these systems for the precipitation and collection of metal precipitates.

Compost (anaerobic) Wetlands — These systems typical contain limestone and composted organic matter in a vegetated substrate. Typical vegetation includes cattails. Most flow is surficial. Sulfate reduction and limestone dissolution occurs within these systems.

Limestone Beds — Beds of limestone that are exposed at the surface. Water level within the beds are below the exposed surface of the limestone. Water flows horizontally through these beds. They are designed for use after iron is removed from the water and are intended to remove manganese by encouraging conditions beneficial for biological manganese oxidation. Usually placed at the end of treatment systems, and can also add additional alkalinity (Rose et al. 2003).

Limestone Ponds — Constructed over upwellings of mine drainage; water flows upward through the limestone. Function similarly to ALDs. Generally used when water has low DO and contains low levels of aluminum and ferric iron.

Open Limestone Channels — Channel or ditch lined with limestone. Usually placed on a slope so the flowing water scours the limestone surface and voids to keep "clean". This system takes into account that limestone may armor with ferric hydroxides, but relies on the premise that armored limestone will continue to dissolve at a slower rate. If a large settling pond is not used at the end of these systems, metal precipitates can enter and damage the watershed (Ziemkiewicz et al. 2003).

Diversion Wells — Cylindrical structures in which a split of a contaminated stream water flows upward through a bed of limestone at a velocity capable of fluidizing the bed. The agitation of the limestone functions to keep the surfaces from armoring. In addition, the limestone fines are generated and carried out of the system into the receiving stream, where they may continue to dissolve and add alkalinity; hence a length of the stream may be sacrificed for downstream improvement in water quality. This system must be filled with the proper size and amount of stone, or bed will collapse and lose effectiveness. Stone must be replenished every few days.

Limestone Sands — This technology utilizes several, large, strategically placed piles of fine limestone within streambeds of a contaminated watershed. Some alkalinity is added during base flow conditions. During storm flow conditions the limestone is transported throughout the watershed where it is incorporated in the stream sediments and dissolved to add alkalinity. Again, a length of the stream may be sacrificed for downstream improvement in water quality. The piles must be replaced at periodic intervals.

RAPS — A reducing and alkalinity producing system . consists of a layer of limestone overlain by a layer of composted organic matter. A drainage system is placed within the limestone layer to force the mine water to flow downward through the compost and limestone. The compost removes dissolved oxygen and reduces ferric iron to ferrous iron to minimize armoring of the limestone. Typically the design includes 2 m of head between the water surface in the RAPS, and the subsequent unit operation accounts for any loss of permeability. These systems are commonly flushed periodically in an attempt to remove precipitated metals and maintain permeability. RAPS are preceded with a pond to for allow precipitation of metals within the pond and not in the RAPS. Aerobic wetlands are used after these systems for the precipitation and collection of metal precipitates.

ReRAPS — Recirculating RAPS, in which alkaline water produced by the RAPS (see above) is mixed with the influent water in a pond to raise pH high enough to precipitate aluminum outside of the RAPS. This water is then pumped to the RAPS. System has been used to treat coal pile runoff where influent water flow is intermittent (Garrett et al. 2002).

Water-Powered Devices — These devices use available head pressure at the site to move some type of device (e.g., wheel, drum, tipping bucket) that meters out an alkaline material. Aerobic wetlands are used after these systems for the precipitation and collection of metal precipitates.

Windmills — These are typically used for aeration by using the power generated from the windmill to pump air through tubing into the mine water. They can also use power to meter out alkaline materials as in water-powered devices.

Sodium Carbonate Briquettes — Na_2CO_3 pressed into briquettes, commonly referred to as soda ash, are placed in a gravity dispenser (hopper) and allowed to dissolve in flowing mine water. Ponds are used after these systems for the precipitation and collection of metal precipitates.

Liquid Sodium Hydroxide — A 20 to 50 percent solution of NaOH, sometimes referred to as “caustic soda”, is stored in a large tank and gravity fed into the mine water. Ponds are used after these systems for the precipitation and collection of metal precipitates.

Hydrated Lime — Calcium hydroxide ($Ca(OH)_2$), usually in powdered form, is added to mine water via a screw feeder. Ponds are used after these systems for the precipitation and collection of metal precipitates.

Quick Lime — Calcium oxide (CaO), requires water to make up slurry (called milk of lime) prior to adding to mine water. Ponds are used after these systems for the precipitation and collection of metal precipitates.

Table 17. Techniques Used for Treating Coal Mine Drainage

Technology	Electricity	Moving Parts	Maintenance Frequency		Frequency of Chemical Addition	Design Life (years)
			Minor	Major		
Aerobic Wetlands Anoxic Limestone Drains Compost Wetlands Limestone Beds Limestone Ponds Open Limestone Channels	N	N	monthly	none anticipated	none	20 - 30
Diversion Wells	N	N	weekly	none	weekly	20 - 30
Limestone Sands	N	N	6 months	6 months	6 months	6 months
RAPS	N	N	monthly	6 months	none	20 - 30
RERAPS	Y	Y	monthly	none	none	20 - 30
Water-Powered Devices Windmills	N	Y	weekly	weekly-yearly	none - monthly	5 - 10
Sodium Carbonate Briquettes Liquid Sodium Hydroxide	N	N	daily	weekly - monthly	daily - monthly	5 - 10
Hydrated Lime Quick Lime	Y	Y	daily	weekly - monthly	daily - monthly	5 - 10

Designing Passive Treatment Systems

Characterizing Mine Drainage Discharges

In order to select the most effective passive treatment unit operations and to size them properly, the untreated mine water must be well characterized. The quality and quantity of some mine discharges are very consistent, while other discharges may vary by orders of magnitudes in both contaminant concentrations and flow. At an absolute minimum, water quality and quantity data should be collected during high and low flow periods. It is recommended that the discharge be monitored periodically (e.g., monthly) for a complete water year. It is best to select the monitoring dates in advance, and follow through on the monitoring regardless of weather. Both the flow rate and chemical composition of a discharge can vary seasonally and in response to storm events. If the passive treatment system is expected to operate during all weather conditions, then the discharge flow rates and water quality should be measured in different seasons and under representative weather conditions.

One of the most important measurements in sizing each passive unit is to obtain an accurate measurement of the total flow of the mine discharge(s) or seep(s). Water samples should be collected at the discharge or seepage point for chemical analysis, which should include pH, alkalinity, iron, manganese, aluminum, and hot acidity (H_2O_2 method) measurements. If an anoxic limestone drain is being considered, and the pH is less than 5, iron concentrations should be speciated into ferric and ferrous. At pH levels above 5, one can assume that all dissolved iron is in the ferrous form. The samples should be analyzed for other ions that are usually present in significant concentrations in coal mine drainage: calcium, magnesium, potassium, sodium, cobalt, nickel, zinc, and sulfate. A cation/anion balance can be calculated to help verify the laboratory analyses (see *Chemical Characteristics of Mine Drainage* on page 12).

In addition, pH, alkalinity, and dissolved oxygen should be measured in the field. If the pH is greater than 4.5, a simple test for determining whether the water is net alkaline should be performed: after recording the pH of the water, collect a sample , and add hydrogen peroxide ; then stir or shake the sample and measure the pH again. If the pH drops below 4.5, the water is net acidic. If the pH remains above 4.5, the water is net alkaline. Very inexpensive hydrogen peroxide (3 percent solution), purchased at a pharmacy or grocery store, can be used. The amount of hydrogen peroxide added to the sample is not critical, 5 to 10 mL per 100 mL of sample is adequate.

Selecting Unit Operations

Water quality for a given discharge will determine the unit operations for designing the most effective passive treatment systema. Table 18 shows three major classifications of mine water quality. Each classification is appropriate for a particular unit operation. Examples of class I (net alkaline) discharges are Penn Allegh, Brinkerton, and Scrubgrass; examples of class II discharges are Elklick, Howe Bridge, and Morrison. (See Table 4.) Class III discharges are Jennings, Schnepp, and REM-R. (See Table 11 and Table 12.)

Table 18. Classification of Mine Discharges

Water Quality Parameter*	**Classification**		
	I	**II**	**III**
pH	> 4.5	-	-
H_2O_2 pH	> 4.5	< 4.5	< 4.5
Net Acidity	< 0	> 0	> 0
Ferric Iron	-	< 1	-
Aluminum	-	< 1	-
Dissolved Oxygen	-	< 1	-
Appropriate Unit Operations	Aerobic Pondsand Wetlands	Anoxic Limestone Drains	Reducing and Alkalinity ProducingSystems

* *pH in standard units, concentrations in mg/L, acidity in mg/L as* $CaCO_3$

Currently, there are several types of unit operations for the treatment of coal mine drainage; however, three of the most effective are aerobic ponds and wetlands, anoxic limestone drains, and reducing and alkalinity-producing systems. In aerobic ponds and wetlands, oxidation reactions occur and metals precipitate primarily as oxides and hydroxides. Most aerobic wetlands contain cattails that grow in a clay or spoil substrate. However, plantless systems (i.e., ponds) have also been constructed and function similarly to those that contain plants. It is recommended that net alkaline water be aerated to the maximum extent possible, conveyed to an aerobic pond and polished with an aerobic wetland.

The ALD is a buried bed of limestone intended to add alkalinity to the mine water. The limestone and mine water are kept anoxic so that dissolution can occur without ferric oxyhydroxides armoring the limestone. ALDs are only intended to generate alkalinity, and must be followed by an aerobic system in which metals are removed through oxidation and hydrolysis reactions.

A RAPS consists of layers of limestone and compost. The water flows down through the compost to remove oxygen and to reduce ferric iron to ferrous iron. The limestone adds alkalinity. Most systems are designed to facilitate the periodic removal of aluminum and iron precipitates by flushing water through the system.

Each of these three passive technologies is appropriate for a particular type of mine water problem, but they are most effectively used in combination with each other. Figure 12 can be used to determine the selection and sequence of unit operations for an effective passive treatment system.

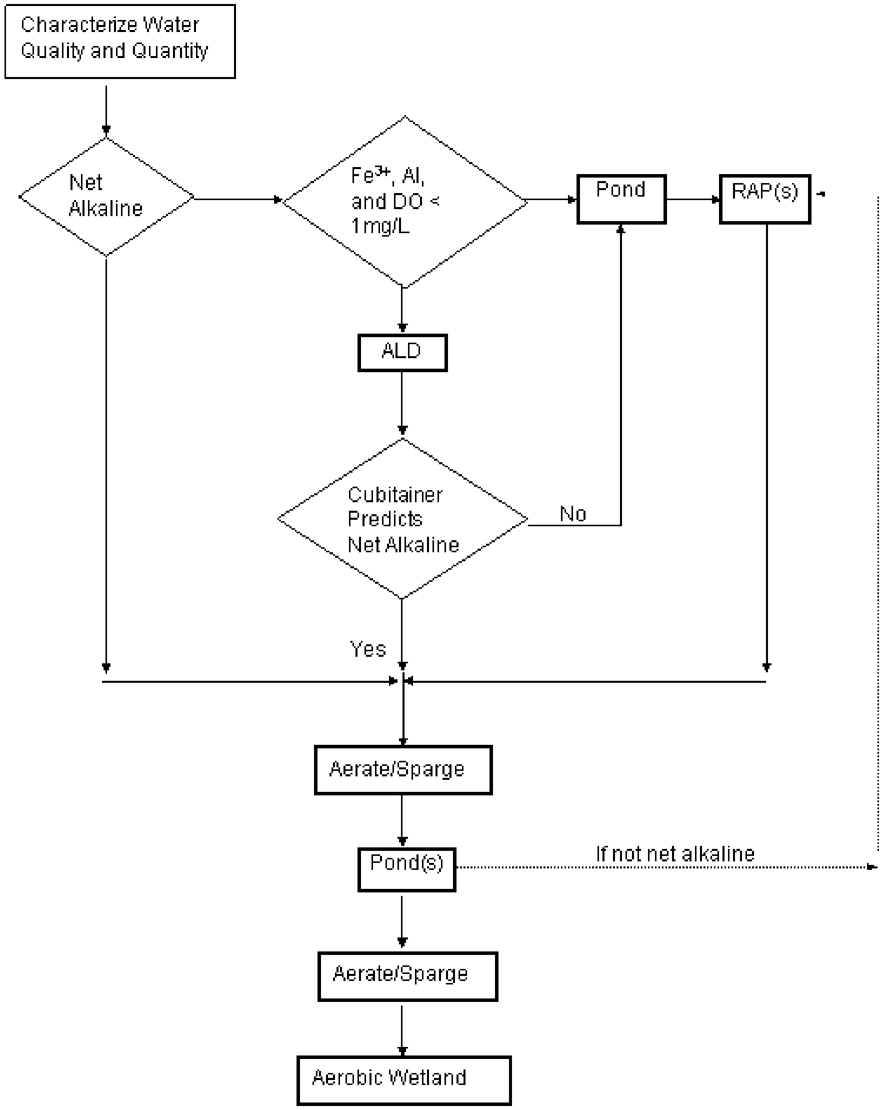

Figure 12. Selection of Passive Treatment Unit Operations

Sizing Passive Systems

The size of the passive treatment system depends on the loading rate of contaminants. Calculate contaminant (iron, manganese, acidity) loads by multiplying contaminant concentrations by the flow rate. If the concentrations are mg/L and flow rates are L/min, the calculation is:

$$\text{Load (g/day)} = \text{Flow (L/min)} \times \text{Concentration (mg/L)} \times 1.44 \text{ (g min/mg day)} \qquad (11)$$

Aerobic Ponds and Wetlands

Sizing criteria for abandoned mined land (AML) uses 20 g d^{-1} m^{-2} for iron, and 1.0 g d^{-1} m^{-2} for manganese. These are intended to cost-effectively decrease contaminant concentrations (Hedin et. Al. 1994a). In many situations at abandoned mined lands, the goal is to improve water quality, not consistently achieve a specific effluent concentration. The AML sizing criteria are based on measurements of contaminant removal by existing constructed wetlands. Most of the removal rates were measured for treatment systems (or parts of treatment systems) that did not consistently lower contaminants to federal effluent standards. In particular, the iron sizing factor for alkaline mine water (20 g d^{-1} m^{-2}) is based on data from six sites, only one of which lowers iron concentrations to compliance.

It is possible that iron removal rates are a function of iron concentration (i.e., as concentrations decrease, the size of the system necessary to remove a unit of iron contamination (e.g., 1 g/d) increases). To account for this possibility, we have provided a more conservative sizing value for systems where the effluent must meet regulatory guidelines. (See Table 1.) We refer to these as “compliance criteria.” The sizing value for iron (10 g d^{-1} m^{-2}) is in agreement with the findings of Stark et al. (1990) for a constructed compost wetland in Ohio that receives marginally acidic water. This rate is still larger, by a factor of 2, than the iron removal rate reported by Brodie et al. (1991) for aerobic systems in southern Appalachia that are regularly in compliance.

The manganese removal rate used for compliance (0.5 g d^{-1} m^{-2}) is based on the performance of five treatment systems, three of which consistently lower manganese concentrations to compliance levels. A higher removal value (1 g d^{-1} m^{-2}), is suggested for AML sites. Because the toxic effects of manganese at moderate concentrations (< 50 mg/L) are generally not significant, except in very soft water (Kleinmann and Watzlaf 1988), and the size of wetland necessary to treat water that contains manganese is so large, AML sites with iron problems should receive a higher priority than those with only manganese problems.

Net alkaline water contains enough alkalinity to buffer the acidity produced by metal hydrolysis reactions. The metal contaminants (iron and manganese) will precipitate, given enough time. The generation of additional alkalinity is unnecessary, so incorporation of limestone or an organic substrate into the passive treatment system is also unnecessary. The goal of the treatment system is to aerate the water and promote metal oxidation processes. In many existing treatment systems where the water is net alkaline, the removal of iron appears to be limited by dissolved oxygen concentrations and pH. Standard features that can aerate the drainage, such as waterfalls or riprap ditches, should be followed by quiescent areas. Aeration only provides enough dissolved oxygen to oxidize about 50 mg/L Fe^{2+}. AML with higher concentrations of Fe^{2+} may require a series of aeration structures and wetland basins. The wetland cells allow time for iron oxidation and hydrolysis to occur, and space in which the iron floc can settle out of suspension. The entire system can be sized based on these iron removal rates. If manganese removal is desired, base the system's size on manganese removal rates. Removal of iron and manganese occurs sequentially in passive systems; if both iron and manganese removal are necessary, add the two wetland sizes together.

Anoxic Limestone Drains (ALD)

The primary chemical factor believed to limit the utility of an ALD is the presence of ferric iron (Fe^{3+}), aluminum (Al^{3+}) and dissolved oxygen. When acidic water containing *any* Fe^{3+} or Al^{3+} contacts limestone, metal hydroxide particulates (FeOOH or $Al(OH)_3$) will form. No oxygen is necessary. Ferric hydroxide will precipitate on and around limestone, limiting further dissolution. It has not been determined if precipitation of aluminum hydroxides limit limestone dissolution. The buildup of both precipitates within the ALD can eventually decrease the drain permeability and cause plugging. The presence of dissolved oxygen in mine water will promote the oxidation of ferrous iron to ferric iron, and the precipitation of solids that may limit limestone dissolution and reduce permeability in the ALD. While the short-term performance of ALDs that receive water containing elevated levels of Fe^{3+}, Al^{3+} or DO can be spectacular (total removal of the metals within the ALD) (Nairn et al. 1991), the long-term performance of these ALDs is not good. (See *Premature Failure of Two ALDs* on page 43.)

Mine water that contains very low concentrations of DO, Fe^{3+} and Al (all < 1 mg/L) is ideally suited for pretreatment with an ALD. As concentrations of these parameters rise above 1 mg/L, the risk that the ALD will fail prematurely also increases. The length of time an ALD operates before failing is a function of these contaminant concentrations; the amount of initial void volume in the ALD, the cross-section of the ALD perpendicular to the flow, and the dissolution rates of limestone (creation of new void volume).

In some cases, the suitability of using an ALD to treat mine water can be evaluated by the type of discharge, and field measurements of pH. Net acidic mine waters that seep from spoils and flooded underground mines and have a field pH ofgreater than 5, characteristically have concentrations of DO, Fe^{3+}, and Al that are all less than 1 mg/L. Such sites are generally excellent candidates for treatment with an ALD. Mine waters that discharge from open drift mines or have pH of less than 5 must be analyzed for Fe^{3+} and Al. Mine waters with pH of greater than 5 can contain dissolved Al and Fe^{3+}. In northern Appalachia, for example, most mine drainages with a pH of less than 3 contain significant concentrations of Fe^{3+} and Al, rendering them inappropriate for treatment with an ALD.

The mass of limestone required to neutralize a certain discharge for a specified period of time (M_t) can be readily calculated from the mine water flow rate and assumptions about the alkalinity-generating performance of the ALD (equations 12 and 13). Research indicates that approximately 15 hours of contact time between mine water and limestone in an ALD is necessary to achieve a maximum concentration of alkalinity. In order to achieve 15 hours of contact time within an ALD, 2,800 kg of limestone is required for each L/min of mine water flow (equation 12). In equation 13, M_c represents the mass of limestone consumed over a period of time. For example, an ALD that discharges water with 300 mg/L of alkalinity (the maximum sustained concentration thus far observed in an ALD effluent), dissolves 1,750 kg of limestone (90 percent calcium carbonate) in ten years, per each L/min of mine water flow. Equations 12 and 13 must be summed to construct an ALD that contains sufficient limestone (90 percent calcium carbonate) to ensure a 15-hour retention time throughout a 20-year period. Therefore, a limestone bed should contain 6,200 kg of limestone for each L/min of flow, which is equivalent to 26 tons of limestone for each gallon per minute of flow. The calculation assumes that the ALD is constructed with 90 percent $CaCO_3$ limestone rock that has a porosity of 49 percent. The calculation also assumes that original mine water does not contain ferric iron or aluminum. The presence of these ions could result in faster rates of limestone dissolution through the generation of acidity during hydrolysis. More importantly, they have the potential to limit limestone dissolution and cause a significant reduction in permeability that could very well lead to failure (as previously discussed). For a more detailed discussion of limestone dissolution rates, see Cravotta and Watzlaf (2002).

$$M_t = (\text{flow x bulk density}_{LS} \text{ x } t_d) / \text{void ratio} \qquad (12)$$

$$M_c = (\text{flow x alkalinity concentration x design lifetime}) / CaCO_3 \text{ content} \qquad (13)$$

There are still some concerns about the ability of ALDs to maintain unchanneled flow for a prolonged period of time, how much of the $CaCO_3$ content of the limestone can be expected to dissolve, whether the ALDs will collapse after significant dissolution of the limestone, and whether inputs of DO that are not generally detectable with standard field equipment (0 to 1 mg/L) might eventually result in armoring the limestone with ferric hydroxides. However, the long-term effectiveness of several of the ALDs discussed here seems to indicate that the above calculations are valid.

The anoxic limestone drain is just one component of a passive treatment system. When an ALD operates ideally, its only effect on mine water chemistry is to raise (or keep) pH to (at) circumneutral levels, and increase concentrations of calcium and alkalinity. Dissolved Fe^{2+} and manganese should be unaffected by flow through the ALD. The ALD must be followed by a settling basin or wetland system in which metal oxidation, hydrolysis and precipitation can occur. The type of post-ALD treatment system depends on the acidity of the mine water and the amount of alkalinity generated by the ALD. If the ALD generates enough alkalinity to transform the acid mine drainage to a net alkaline condition, then the ALD effluent can be treated with an aerobic pond and wetland. If possible, the water should be aerated as soon as it exits the ALD and directed into a settling pond. An aerobic wetland should follow the pond. The total post-ALD system should be sized according to the criteria provided earlier for net alkaline mine water. At this time, it appears that mine waters with acidity concentrations less than 150 mg/L are readily treated with an ALD and aerobic wetland system.

If the mine water is contaminated with only Fe^{2+} and manganese, and the acidity exceeds 300 mg/L, it is unlikely that an ALD constructed using current practices will discharge net alkaline water. When this partially neutralized water is treated aerobically, the iron will precipitate rapidly, but the absence of sufficient buffering can result in a discharge with low pH. Building a second ALD to recharge the mine water with additional alkalinity after it flows out of the aerobic system is currently not feasible because of the high dissolved oxygen content of water flowing out of aerobic systems. If the treatment goal is to neutralize all of the acidity passively, then a RAPS should be built to generate additional alkalinity. Such a treatment system thus contains all three passive technologies. The mine water flows through an ALD, into an aerobic pond and wetland, and then into a RAPS, followed by another pond and wetland.

If the mine water is contaminated with ferric iron (Fe^{3+}) or aluminum, higher concentrations of acidity can be treated with an ALD than when the water is contaminated with only Fe^{2+} and manganese. This enhanced performance results from a decrease in mineral acidity due to the hydrolysis and precipitation of Fe^{3+} and aluminum within the ALD. These metal-removing reactions decrease the mineral acidity of the water. ALDs constructed to treat mine water contaminated with Fe^{3+} and aluminum and having acidity greater than 1,000 mg/L have discharged net alkaline water. The long-term prognosis for these metal-retaining systems is not good. However, even if calculations of system longevity (as described above) are inaccurate for waters contaminated with Fe^{3+} and aluminum, their treatment with an ALD maybe cost-effective in some instances, when compared to chemical alternatives (Skousen and Faulkner 1992).

When a mine water is contaminated with Fe^{2+} and manganese and has an acidity between 150 mg/L and 300 mg/L, the ability of an ALD to discharge net alkaline water will depend on the concentration of alkalinity produced by the limestone system. The amount of alkalinity generated by a properly constructed and sized ALD depends on the chemical characteristics of the mine water. An experimental method has been developed that results in an accurate assessment of the amount of alkalinity being generated when a particular mine water contacts a particular limestone (Watzlaf and Hedin 1993). The method involves the anoxic incubation of the mine water in a container (cubitainer) filled with limestone gravel. This cubitainer test may be used in the design of passive systems, as outlined in Figure 12. The cubitainer test can determine if the ALD will impart sufficient alkalinity to allow for the ALD effluent to be treated with ponds and wetlands, or if the water needs additional treatment (RAPS) to add alkalinity. In experiments at two sites, the concentration of alkalinity that developed in these containers after 48 hours correlated very well with the concentrations of alkalinity measured in the ALD effluents.

Reducing and Alkalinity-Producing Systems (RAPS)

Based on the results of this study, RAPS were found to remove 40 g d^{-1} m^{-2} of acidity for the initial system, and 15 g d^{-1} m^{-2} for the second RAPS in series. It is important to note that these values were obtained from systems of similar construction, having compost layers about 0.2 m thick and limestone layers 0.4 to 0.9 m thick. If thinner layers were used, these surface area-based acidity removal rates may not be applicable. It is reasonable to expect that alkalinity production will be dependent on influent water quality. Jage et al. (2000) found that alkalinity production in RAPS significantly correlated with detention time, influent total iron concentrations, and non-manganese acidity concentrations. Rose and Dietz (2002) found positive correlations between alkalinity production and influent iron and hydrogen ion concentrations, and detention time in the compost. They also found acidity removal rates of 25 - 50 g d^{-1} m^{-2} for the 12 systems that they studied, and suggested using 25 g d^{-1} m^{-2} as a design criteria for RAPS. Thomas and Romanek (2002) found alkalinity generation rates averaged 88 $gd^{-1}m^{-2}$ in pilot scale studies using compost amended with fine-grained limestone (~1.2 mm). Based on these findings, it is probably prudent to use a sizing criteria of 25 - 30 g d^{-1} m^{-2} for the first RAPS in a series, and 15 g d^{-1} m^{-2} for a subsequent system. It is also recommended that the limestone layer contain enough limestone to theoretically retain the water for 15 hours throughout the design life of the system (6,200 kg of limestone per L/min of flow), the same sizing criteria used for an ALD.

Constructing Passive Systems

Aerobic Ponds/Wetlands

A typical aerobic wetland is constructed by planting cattail rhizomes in soil or alkaline spoil obtained onsite. Some systems have been planted simply by spreading cattail seeds, with good plant growth after two years. The depth of the water in a typical aerobic system is 10 to 50 cm. Ideally, a cell should not be of a uniform depth, but should include shallow and deep marsh areas and a few deep (1 to 2 m) spots. Note that common rooted aquatic vegetation cannot tolerate water depths greater than 50 cm, and require shallower depths for propagation.

Typically, a pond is situated before the wetland to remove a majority of the iron hydroxides. This pond is usually sized for an 8 to 24 hour retention time and is typically 1.5 to 2.5 m deep. To account for accumulations of iron, the value 0.17 g of iron per cm^3 can be used so that the required detention time will be available for a predetermined time (i.e., its design life). It is recommended that the freeboard of aerobic wetlands/ponds be constructed at about 1 m for the removal of iron. Observations of sludge accumulation in existing wetlands suggest that a 1-m freeboard should be adequate to hold 20 to 25 years of FeOOH accumulation. We have achieved good success when the pond and wetland have similar surface areas. This allows for future removal of iron oxides from the pond without disturbing the vegetated wetland. Recently iron oxides have been characterized for potential recycling (e.g., as pigments) (Kairies et al. 2001, Hedin 2002).

Often, several wetland cells and/or ponds are connected by flow through a v-notch weir, lined railroad tie steps, or down a ditch. Use of multiple cell/ponds can limit the amount of short-circuiting, and aerates the water at each connection. If there are elevation differences between the cells, the interconnection design should dissipate kinetic energy to avoid erosion and/or the mobilization of precipitates. Spillways should be designed to pass the maximum probable flow. Spillways should consist of wide cuts in the dike with side slopes no steeper than 2H:1V, be lined with non-biodegradable erosion control fabric and a coarse riprap, if high flows are expected (Brodie 1991). Proper spillway design can preclude future maintenance costs associated with erosion and/or failed dikes. If pipes are used, small diameter (< 30 cm) pipes should be avoided, because they can plug with litter and FeOOH deposits. Pipes should be made of PVC, PE or coated for long-term stability. More details on the construction of aerobic wetland systems can be found in Hammer’s *Creating Freshwater Wetlands*, (1992) .

The floor of the wetland cell may be sloped up to a 3 percent grade. If a level cell floor is used, then the water level and flow are controlled by the downstream dam spillway and/or adjustable riser pipes.

As discussed previously, some of the aerobic systems that have been constructed to treat alkaline mine water have little emergent plant growth and are better termed ponds than wetlands. Metal removal rates in these plantless, aerobic systems appear to be similar to what is observed in aerobic systems that contain plants. However, plants may provide value not reflected in measurements of contaminant removal rates. For example, plants can facilitate the filtration of particulates, prevent flow channelization and provide wildlife benefits that are valued by regulatory and environmental groups.

ALDs

In an ALD, alkalinity is produced when the acidic water contacts the limestone in an anoxic, closed environment. Limestone with higher $CaCO_3$ content (> 80 percent) has been shown to dissolve faster than limestone with a higher $MgCO_3$ or $CaMg(CO_3)_2$ content (~50 percent $CaCO_3$) (Watzlaf and Hedin 1993). The limestone used in most successful ALDs have 80 to 95 percent $CaCO_3$ content. Most effective systems have used 5- to 20-cm-sized limestone. Some systems constructed with fine and small gravel limestone have failed, apparently because of plugging problems. The ALD must be sealed so that the inputs of atmospheric oxygen are minimized, and the accumulation of carbon dioxide within the ALD is maximized. This is usually accomplished by burying the ALD under 1 to 3 m of clay. Plastic is sometimes placed between the limestone and clay as an additional gas barrier. In some cases, the ALD has been completely wrapped in plastic before burial (Skousen and Faulkner 1992). This can also help keep clay and dirt from getting into the pore volume from the bottom and sides of the excavation. The ALD should be designed to inundate the limestone with water at all times. Clay dikes within the ALD or riser pipes at the outflow of the ALD will help ensure inundation.

The dimensions of existing ALDs vary considerably. (See Table 7.) Narrower ALDs have the advantage of minimizing short-circuiting, but present a small cross-section perpendicular to the flow that may be more prone to clogging. Wider ALDs may be less likely to suffer significant permeability reductions (clogging) but may allow short circuiting to occur. In the end, however, site conditions will often dictate the dimensions of the ALD.

RAPS

RAPS are commonly constructed with a 1-m thick layer of limestone. A network of perforated pipes is placed in the bottom of this limestone layer. On top of the limestone, a layer of organic matter is placed that is typically 15 to 60 cm thick. Spent mushroom compost, which is readily available and affordable in and around Pennsylvania, is an often used organic material. Most spent mushroom compost consists of horse manure, hay, straw, chicken manure and gypsum. Mine water flows down through the system, encountering the reducing environment of the compost before contacting the limestone. The compost layer is intended to remove the dissolved oxygen and convert any ferric iron to the ferrous state to avoid armoring of the limestone. It is thought that RAPS may be less prone to aluminum plugging than ALDs because of their larger cross-section (perpendicular to flow paths) and higher available head pressures. The systems are generally constructed to allow for at least 2 m of head to be utilized, if needed, to overcome losses in permeability. Alkalinity generation rates for these systems range from 40 to 60 g per day per m^2 of surface area for the first RAPS, and from 15 to 20 g per day per m^2 of surface area for a second RAPS, when two RAPS are used in series (Watzlaf et al. 2000). Both iron and aluminum are removed within these systems. Most are periodically flushed to extend the life of these systems. No guidelines have yet been developed to guide the frequency, duration, or intensity of the flushes.

A pond should be used to oxidize, precipitate and settle iron before the water enters the RAPS to minimize the accumulation of iron precipitates (and other settleable solids) on top of the compost layer in the RAPS. This pond will also serve as an equalization basin. The size of this pond is site specific, but should be larger at sites where the pH of influent water is above 3.5. Once the pH drops below ~ 3.0, iron is removed much more slowly from mine drainage.

Operation and Maintenance

Operational problems with passive treatment systems can be attributed to inadequate design, unrealistic expectations, pests, inadequate construction methods, or natural problems. If properly designed and constructed, a passive treatment system can be operated with a minimum amount of attention and money.

Probably the most common maintenance problem is stability in the dike and spillway. Reworking slopes, rebuilding spillways, and increasing freeboard can all be avoided by proper design and construction using existing guidelines for such construction.

Pests can plague wetlands with operational problems. Muskrats will burrow into dikes, causing leakage and potentially catastrophic failure problems, and can also uproot significant amounts of cattails and other aquatic vegetation. Muskrats can be discouraged by lining dikes and slopes with chain link fence or riprap to prevent burrowing (Brodie 1990). Beavers dams cause water level disruptions and can seriously damage vegetation. They are very difficult to control once established. Small diameter pipes traversing wide spillways (three-log structure) and trapping have had limited success in beaver control. Large pipes with 90-degree elbows on the upstream end have been used as discharge structures in beaver-prone areas (Brodie 1991). Otherwise, shallow ponds with dikes and shallow slopes toward wide, riprapped spillways may be the best design to deter beaver populations.

Insects, such as the armyworm, with their appetite for cattails, have devastated monocultural wetlands (Hedin, et al. 1994a). The use of various plants in a system will minimize such problems. Mosquitos can breed in wetlands where mine water is alkaline. In southern Appalachia, mosquito fish (*Gambusia affinis*) have been introduced into alkaline-water wetlands to control mosquito populations.

Conclusions

Characterization of influent water quality and quantity, including seasonal variation, is important prior to the selection and development of a passive treatment system (Hyman and Watzlaf 1995.). The presence or absence of periodic events, such as spring flushes of deposited metal salts from within the mine area, may influence the selection and sizing of passive systems.

Aerobic ponds and wetlands can be very effective for the removal of iron from net alkaline mine water. It appears that the original estimate of Hedin et al. (1994a) of 10 to 20 g d^{-1} m^{-2} remains a convenient pre-construction rule-of-thumb for estimating pond and wetlands sizes. Recent studies have provided insight into the factors that control the overall processes, and these approaches may be used to fine-tune sizing criteria. Modeling has concluded that aeration to sparge carbon dioxide and increase pH can significantly increase iron oxidation rates, thereby reducing the size of aerobic ponds and wetlands needed for iron removal.

ALDs can effectively treat net acidic mine water. The ideal influent water quality for an ALD is net acidic water with a pH above 5.0. At this pH, neither ferric iron nor aluminum are soluble in significant quantities. Intercepted ground water is typically low in dissolved oxygen, and often contains partial pressures of carbon dioxide higher than atmospheric levels, which allows for development of alkalinity concentrations greater than 100 mg/L as $CaCO_3$. Near maximum levels of alkalinity (usually between 150 and 300 mg/L) can be achieved with 15 hours or more of contact time. ALDs are tolerant of both ferrous iron and manganese, because they remain soluble within the ALD. However, the presence of ferric iron, and particularly aluminum, can reduce permeability of the ALD by precipitation of these metals within the voids in the limestone. This has been documented in an ALD (Jennings) that received 21 mg/L of aluminum and clogged within eight months. In the absence of ferric iron and aluminum, ALDs have continued to perform well with no obvious seasonal variation or long-term reduction in effectiveness.

Tracer studies indicated that while ALDs approximate plug-flow systems, some short circuiting occurs, and dead areas do exist. Calculated detention times, using 49 percent porosity, were in fairly good agreement with the median detention times of the tracer tests.

Water quality data determine the applicability of an ALD and flow data provide the basis for sizing an effective ALD for the desired design life. At mine sites where the appropriate water quality criteria were met and the ALD was sized properly, effective treatment of mine drainage occurred, provided that the ALD was followed by ponds and/or wetlands for iron oxidation, precipitation, and settling. At these sites, it is projected that the ALD will be effective for the designed lifetime of 25 to 30 years and, in some cases, well beyond.

ALDs offer an effective means of introducing alkalinity into net acidic waters that contain neither ferric iron nor aluminum. The presence of either of these ions will reduce permeability of the ALD by precipitation, which will cause premature failure by clogging. In the absence of these ions, ALDs have continued to perform well with no obvious seasonal variation nor long-term degradation. Near maximum levels of alkalinity (usually between 150 and 300 mg/L) can be achieved with 15 hours or more of contact time. ALDs are tolerant of both ferrous iron and manganese. ALDs must be viewed as a unit operation, not a standalone remediation technique, and must be followed by a pond and wetland for iron oxidation, precipitation, and settling.

Alkaline addition in a RAPS is dominated by the limestone dissolution pathway. The acid neutralization potential afforded by a RAPS ranges from 35 to over 400 mg/L $CaCO_3$. Sulfate reduction contributed an average of 28 percent (with a range of 5 to 51 percent) of the total alkalinity produced in the system. The rate of alkaline addition for a single RAPS is about 40 to 60 g d^{-1} m^{-2}. Rates for the second RAPS in a series fall off to about 1/2 to 1/3 of the rate of the first system. Much of the variability in performance can be attributed to influent water quality and detention time. As with ALDs, RAPS should be viewed as unit operations, not stand-alone technologies. They must be preceded by a pond/wetland to precipitate iron and other settleable solids. As with ALDs, RAPS must also be followed by a pond and wetland for iron oxidation, precipitation, and settling.

Care should be taken to obtain sufficient water quality data of the target drainage, including seasonal variation, before desiging and developing a passive treatment system. Site and funding constraints may limit the applicability of passive techniques for some mine drainages. However, for those drainages with appropriate water quality and land availability, passive treatment systems continue to perform very well.

Abbreviations and Acronyms

ALD	anoxic limestone drain
AML	abandoned mined land
AASHTO	American Association of State Highway and Transportation Officials
atm	atmosphere
Eh	oxidation-reducing potential
Ha	hectare
ICAP-AES	inductively-coupled argon plasma –atomic emission spectroscopy
ISE	ion selective electrode
L	liter
L/min	liters per minute
mL	mililiter
mg/L	miligram per liter
RAPS	reducing and alkalinity-producing systems
SRB	sulfate reducing bacteria
s.u.	standard units
µm	micrometer

References

American Public Health Association. 1985. *Standard Methods for the Examination of Water and Wastewater*. Washington, DC: American Public Health Association. 1,268 pp.

American Public Health Association. 1998. *Standard Methods for the Examination of Water and Wastewater*. Washington, DC: American Public Health Association. 1,162 pp.

Barnes, H. L. and S. B. Romberger. 1968. Chemical Aspects of Acid Mine Drainage. *J. Water Pollution Control Federation.* 40:370-384.

Batty, L. C. and P. L. Younger. 2002. Critical Role of Macrophytes in Achieving Low Iron Concentrations in Mine Water Treatment Wetlands. *Envir. Sci. Technol*. 36:3,997-4,002.

Beck, J. V. and D. G. Brown. 1968. Direct Sulfur Oxidation in the Solubilization of Sulfide Ores by Thiobaccillus Ferrooxidans. *J. Bacteriology*. 96:1,433-1,434.

Brodie, G. A., Britt, C. R., Tomaszewski, T. M., and H. N. Taylor. 1991. Use of Passive Anoxic Limestone Drains to Enhance Performance of Acid Drainage Treatment Wetlands. *Proceedings of Reclamation 2000: Technologies for Success* (Durango, CO). pp. 211-222.

Brodie, G. A. 1990. Treatment of Acid Drainage Using Constructed Wetlands: Experiences of the Tennessee Valley Authority. *Proceedings of the 1990 National Symposium on Mining* (Lexington, KY). pp. 77-83.

Brodie, G. A. 1991. Achieving Compliance with Staged Aerobic Constructed Wetlands to Treat Acid Drainage. *Proceedings of the 1991 National Meeting of the American Society of Surface Mining and Reclamation* (Princeton, WV). pp. 151-174.

Brown, M., Barley, B., and H. Wood. 2002. *Minewater Treatment: Technology, Application and Policy*. Dorchester, United Kingdom: IWA Publishing. 453 pp.

Butler, J. N. 1991. *Carbon Dioxide Equilibria and Their Applications*. Chelsea, MI: Lewis Publishers. 259 pp.

Cravotta, C. A. III and G. R. Watzlaf. 2002. Design and Performance of Limestone Drains to Increase pH and Remove Metals from Acidic Mine Drainage. In: *Handbook of Groundwater Remediation Using Permeable Reactive Barriers.*USA: Elsevier Science. pp. 19-66.

Davies, S. H. and J. J. Morgan. 1989. Manganese (II) Oxidation Kinetics on Metal Oxide Surfaces. *J. Colloid and Interface Science.* 129:63-77.

Dempsey, B. A., Roscoe, H. C., Ames, R., Hedin, R., and B.-H. Jeon. 2001. Ferrous Oxidation Chemistry in Passive Abiotic Systems for Treatment of Mine Drainage. *Geochemistry: Exploration, Environment and Analysis.* 1(1):81-88.

Diehl, D. and W. Stumm. 1984. Is Dissolved Mn^{2+} Being Oxidized by O_2 in Absence of Mn-Bacteria or Surface Catalysts. *Geochemica et. Cosmochimica Acta.* 48:1,571-1,573.

Dietz, J. M. and B. A. Dempsey. 2001. Treatment of Mine Drainage Ising Recirculated Iron Oxides in a Complete Mix Reactor. *Proceedings of the 2001 Annual Conference of the National Association of Abandoned Mine Land Programs* (Athens, Ohio). pp. 1-14.

Duncan, D., Landesman, J. and C. Walden. 1967. Role of Thiobaccillus Ferrooxidans in the Oxidation of Sulfide Minerals. *Canadian J. Microbiology*. 13:377-403.

Ehrlich, H. L. *Geomicrobiology*. New York: Dekker. 1981, 393 pp.

Fales, H. A. and F. Kenny. 1940. *Inorganic Quantitative Analysis*. New York: D. Appleton Century Co. 713 pp.

Garrett, W. E., A. A. Bartolucci, Pitt, R. R. and M. E. Vermace. 2002. Recirculating – Reducing and Alkalinity Producing System (RERAPS) for the Treatment of Acidic Coal Pile Runoff. *Proceedings of the 2002 National Meeting of the American Society of Mining and Reclamation* (Lexington, KY). pp. 539 - 557.

Gerber, D. W., Burris, J. E. and R. W. Stone. 1985. Removal of Dissolved Iron and Manganese Ions from Water by a Sphagnum Moss System. *Proceedings of Wetlands and Water Management on Mined Lands* (University Park, PA). pp. 365-372.

Girts, M. A., Kleinmann, R. L. P. and P. M. Erickson. 1987. Performance Data on Typha and Sphagnum Wetlands Constructed to Treat Coal Mine Drainage. *Proceedings of the 8th Annual Surface Mine Drainage Task Force Symposium* (Morgantown, WV).

Groudev, S. 1979. Mechanism of Bacterial Oxidation of Pyrite. *Mikrobiologija*. (16)75-87.

Hammack, R. W., Dvorak, D. H. and H. M. Edenborn. 1993. The Use of Biogenic Hydrogen Sulfide to Selectively Recover Metals from a Severely Contaminated Mine Drainage. In: *Proceedings of the International Biohydrometallurgy Symposium* (Jackson Hole, WY).

Hammer, D. A. 1992. *Creating Freshwater Wetlands*. Boca Raton, FL: Lewis Publishers. 298 pp.

Hedin, R. S., Hyman, D. M. and R. W. Hammack. 1988. *Implications of Sulfate Reduction and Pyrite Formation Processes for Water Quality in a Constructed Wetland: Preliminary Observations*. U.S. Bureau of Mines IC 9183. pp. 382-388.

Hedin, R. S., Dvorak, D. H., Gustafson, S. L., Hyman, D. M., McIntire, P. E., Nairn, R. W., Neupert, R. C., Woods, A. C., and H. M. Edenborn. 1991. *Use of a Constructed Wetland for the Treatment of Acid Mine Drainage at the Friendship Hill National Historic Site, Fayette County, PA*. Interagency Agreement #4000-5-0010. 128 pp.

Hedin, R. S., Nairn, R. W. and R. L. P. Kleinmann. 1994a. *Passive Treatment of Coal Mine Drainage*. U.S. Bureau of Mines IC 9389. 35 pp.

Hedin, R. S. and G. R. Watzlaf. 1994. The Effects of Anoxic Drains on Mine Water Chemistry. *Proceedings of the International Land Reclamation and Mine Drainage Conference and the Third International Conference of the Abatement of Acidic Drainage, Volume 1* (Pittsburgh, PA). U.S. Bureau of Mines Special Publication SP 06B-94. pp. 185-194.

Hedin, R. S., Watzlaf, G. R. and R. W. Nairn. 1994. Passive Treatment of Acid Mine Drainage with Limestone. *J. Environmental Quality*. 23(6):1,338-1,345.

Hedin, R.S. 2002. Recovery of Marketable Iron Oxide from Mine Drainage. *Proceedings of the 2002 National Meeting of the American Society of Mining and Reclamation* (Lexington, KY). pp. 517 – 526.

Hem, J. D. 1985. *Study and Interpretation of the Chemical Characteristics of Natural Water*, 3rd Edition. U.S. Geological Survey Water Supply Paper 2254. 263 pp.

Huntsman, B. E., Solch, J. G. and M. D. Porter. 1978. Utilization of Sphagnum Species Dominated Bog for Coal Acid Mine Drainage Abatement. *Abstracts from the Geological Society of America 91st Annual Meeting* (Toronto, Ontario, Canada). p. 322.

Huntsman, B. E., Kleinmann, R. L. P. and T. O. Tiernan. 1985. Hydrologic and Geochemical Considerations in Maintaining Man-Made Wetlands Constructed for Acid Mine Drainage Abatement. Presented at Wetlands and Water Management on Mined Lands (Penn State University, University Park, PA).

Hyman, D. M. and Watzlaf. 1995. Mine Drainage Characterization for the Successful Design and Evaluation of Passive Treatment Systems. *Proceedings of the 17th Annual Association of Abandoned Mine Lands Conference*. (French Lick, IN). pp. 170-185.

Jage, C. R., Zipper, C. E., and A. C. Hendricks. 2000. Factors Affecting Performance of Successive Alkalinity-Producing Systems. *Proceedings of the 2000 National Meeting of the American Society of Surface Mining and Reclamation* (Tampa, FL). pp. 451-458.

Jennings Water Quality Improvement Coalition. 1999. P*assive Treatment of Acid Mine Drainage, Vertical Flow System*. Final Report for Project 18 of US EPA FY96 Section 319 Grant.

Kairies, C. L., Watzlaf, G. R., Hedin, R. S., and R. C. Capo. 2001. Characterization and Resource Recovery Potential of Precipitates Associated with Abandoned Coal Mine Drainage. *Proceedings of the 2001 National Meeting of the American Society for Surface Mining and Reclamation* (Albuquerque, NM). pp. 278-279.

Kepler, D. A. and E. C. McCleary. 1994. Successive Alkalinity-Producing Systems (SAPS) for the Treatment of Acid Mine Drainage. P*roceedings of the International Land Reclamation and Mine Drainage Conference and the Third International Conference of the Abatement of Acidic Drainage, Volume 1* (Pittsburgh, PA). U.S. Bureau of Mines Special Publication SP 06B-94. pp. 195-204.

Kepler, D. A. 1995. Successive Alkalinity-Producing Systems (SAPS). *Proceedings of the West Virginia Surface Mine Drainage Task Force Symposium* (Morgantown, WV).

Kepler, D. A. and E. C. McCleary. 1997. Passive Aluminum Treatment Successes. *Proceedings of the West Virginia Surface Mine Drainage Task Force Symposium* (Morgantown, WV).

Kirby, C. S., and J. A. Elder Brady. 1998. Field Determination of Fe^{2+} Oxidation Rates in Acid Mine Drainage Using a Continuously Stirred Tank Reactor. *Applied Geochemistry*. 13:509-520.

Kirby, C. S., H. M. Thomas, G. Southman and R., Donald. 1999. Relative Contributions of Abiotic and Biological Factors in Fe(II) Oxidation in Mine Drainage. *Applied Geochemistry.* 14:511-530.

Kirby, C. S. 2002. Problems in acidity and alkalinity measurements in mine drainage. *Proceedings of the 2002 National Meeting of the American Society of Mining and Reclamation*. (Lexington, KY), pp. 1068 - 1071.

Kleinmann, R. L. P. 1979. The Biogeochemistry of Acid Mine Drainage and a Method to Control Acid Formation. PhD Thesis, Princeton University. 104 pp

Kleinmann, R. L. P. 1985. *Treatment of Acidic Mine Water by Wetlands*. U.S. Bureau of Mines IC 9027. pp. 48-52.

Kleinmann, R. L. P., Crerar, D. A., and R. R. Pacelli. 1981. Biochemistry of Acid Mine Drainage and a Method to Control Acid Formation. *Mining Engineering*. 33:300-306.

Kleinmann, R. L. P. and G. R. Watzlaf. 1988. Should the Effluent Limits for Manganese be Modified? In: *Proceedings of the Mine Drainage and Surface Mine Reclamation Conference, Volume II: Mine Reclamation, Abandoned Mine Lands and Policy Issues* (Pittsburgh, PA). U.S. Bureau of Mines IC 9184. pp. 305-310.

Kleinmann, R. L. P., Jones, J. R. and P. M. Erickson. 1988. An Assessment of the Coal Mine Drainage Problem. *Proceedings of the 10th Annual Conference of the Association of Abandoned Mine Land Programs* (Wilkes-Barre, PA). pp. 1-9.

Kleinmann, R. L. P., Tiernan, T. O., Solch, J. G. and R. L. Harris. 1983. A Low-Cost, Low-Maintenance Treatment System for Acid Mine Drainage Ising Sphagnum Moss and Limestone. *Proceedings of the 1983 Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation* (University of Kentucky, Lexington, KY). pp. 241-245.

Luther, G. W. III. 1987. Pyrite Oxidation and Reduction: Molecular Orbital Theory Considerations. *Geochemica et Cosmochimica Acta.* 53:3,193-3,200.

McIntire, P. E. and H. M. Edenborn. 1990. The Use of Bacterial Sulfate Reduction in the Treatment of Drainage from Coal Mines. *Proceedings of the 1990 Mining and Reclamation Conference and Exhibition* (West Virginia University, Morgantown, WV). pp. 409-415.

McKnight, D. M., B. A. Kimbell and R. L. Runkel. 2001. pH Dependence of Iron Photoreduction in a Rocky Mountain Stream Affected by Acid Mine Drainage. *Hydrological Processes.* 15:1,979-1,992.

Nairn, R. W., Hedin, R. S. and G. R. Watzlaf. 1992. Generation of Alkalinity in an Anoxic Limestone Drain. *Achieving Land Use Potential Through Reclamation.* (Proc. Conf. of the 9th National American Society for Surface Mining and Reclamation Meeting, Princeton, WV). pp. 206-219.

Nairn, R. W., Hedin, R. S. and G. R. Watzlaf. 1991. A Preliminary Review of the Use of Anoxic Limestone Drains in the Passive Treatment of Acid Mine Drainage. *Proceedings of the 12th Annual West Virginia Surface Mine Drainage Task Force Symposium* (Morgantown, WV).

Nawrot, J. 1990. Mine Drainage Treatment through Enhanced Biological Sulfate Reduction within Wetlands. *Proceedings of the 1990 Mining and Reclamation Conference and Exhibition*. Vol. II. pp. 353-364.

Nealson, K. H. 1983a. The Microbial Iron Cycle. *Microbial Geochemistry*, W. E. Krumbein, Ed. Boston, MA: Blackwell Scientific. , pp. 159-190.

Nealson, K H. 1983b. The Microbial Manganese Cycle. *Microbial Geochemistry*. W. E. Krumbein, Ed. Boston, MA: Blackwell Scientific. pp. 159-190.

Nordstrom, D. K. and J. W. Ball. 1986. The Geochemical Behavior of Aluminum in Acidified Surface Waters. *Science.* 232:54-56.

Nuttall, C. A, and P. L. Younger. 2000. Zinc Removal from Hard, Circum-Neutral Mine Waters Using a Novel Closed-Bed Limestone Reactor. *Water Research*. 34:1,262-1,268.

PIRAMID Consortium. 2003. *Engineering Guidelines for the Passive Remediation of Acidic and/or Metalliferous Mine Drainage and Similar Wastewaters.* Report European Commission 5th Framework RTD Project No. EVK1-CT-1999-000021. University of Newcastle Upon Tyne, Newcastle Upon Tyne UK. 166 pp.

Postgate, J. R. 1984. *The Sulphate-Reducing Bacteria*. 2nd d. NY: Cambridge University Press. 208 pp.

Robbins E.I., Nord, G. L. Jr., Savela, C. E., Eddy, J. L., Livi, K. J., Gullett, C. D., Nordstrom, D. K., Chou, I. M. and K. M. Briggs. 1996. Microbial and Mineralogical Analysis of Aluminum-Rich Precipitates that Occlude Porosity in a Failed Anoxic Limestone Drain, Monongalia County, West Virginia. *Proceedings of the 13th Annual International Pittsburgh Coal Conf, Volume 2.* (Pittsburgh, PA). p. 761-765

Rose, A. W. and J. M. Dietz. 2002. Case Studies of Passive Treatment Systems: Vertical Flow Systems. *Proceedings of the 2002 National Meeting of the American Society of Mining and Reclamation* (Lexington, KY). pp. 776-797.

Rose, A. W., P. J. Shah and B. Means. 2003. Case Studies of Limestone-Bed Passive Systems for Manganese Removal from Acid Mine Drainage. *Proceedings of the 2003 National Meeting of the American Society for Mining and Reclamation* (Billings, MT). pp. 1,059-1,078.

Sencindiver, J. C. and D. K. Bhumbla. 1988. Effects of Cattails (*Typha*) on Metal Removal from Mine Drainage. 1*988 Mine Drainage and Surface Mine Reclamation, Volume I: Mine Water and Mine Waste*. U.S. Bureau of Mines IC 9183. pp. 359-369.

Silverman, M. P. 1967. Mechanisms of Bacterial Pyrite Oxidation. *J. Bacteriology*. 94:1,046-1,051.

Simmons, J., Ziemkiewicz, P. and D. C. Black. 2002. Use of Steel Slag Leach Beds for the Treatment of Acid Mine Drainage. *Mine Water and the Environment.* 21(2):91-99.

Singer, P. C. and W. Stumm. 1970a. *Oxygenation of Ferrous Iron*. Water Pollution Control Research Series. Federal Water Quality Administration. 14010-06169. 183 pp.

Singer, P.C. and W. Stumm. 1970b. Acidic Mine Drainage: the Rate Determining Step. *Science.* 167:1,121-1,123.

Skousen, J. and B. Faulkner. 1992. Preliminary Results of Acid Mine Drainage Treatment with Anoxic Limestone Drains in West Virginia. *Proceedings of the 13th Annual West Virginia Surface Mining Drainage Task Force Symposium* (Morgantown, WV).

Spratt, A. K. and R. K. Wieder. 1988. Growth Responses and Iron Uptake in Sphagnum Plants and their Relations to Acid Mine Drainage (AMD) Treatment. *Mine Drainage and Surface Mine Reclamation, Volume I: Mine Water and Mine Waste*. U.S. Bureau of Mines IC 9183. pp. 279-286.

Stark, L., E. Stevens, H. Webster and W. Wenerick. 1990. Iron Loading, Efficiency, and Sizing in a Constructed Wetland Receiving Mine Drainage. Paper in *Proceedings of the 1990 Mining and Reclamation Conference and Exhibition: Volume II*, J. Skousen, J. Sencindiver and D. Samuel, Eds. pp. 393-401.

Stone, R. W and B. J. Pesavento. 1985. Micro- and Macro-Biological Characteristics of Wetlands Removing Iron and Manganese.*Proceedings of Wetlands and Water Management on Mined Lands* (Pennsylvania State University, University Park, PA). p. 373.

Stumm, W. and J. Morgan. 1981. *Aquatic Chemistry*.New York: Wiley-Interscience. 583 pp.

Stumm, W. and J. Morgan. 1996. *Aquatic Chemistry*.New York: Wiley & Sons. 1,022 pp.

Temple, K. G. and E. W. Delchamps. 1953. Autotrophic Bacteria and the Formation of Acid in Bituminous Coal Mines. *Applied Microbiolog.*, 1:255-258.

Thomas, R. C. and C. S. Romanek. 2002. Acid Rock Drainage in a Vertical Flow Wetland I: Acidity Neutralization and Alkalinity Generation.*Proceedings of the 2002 National Meeting of the American Society of Mining and Reclamation* (Lexington, KY).

Turner, D. and D. McCoy. 1990. Anoxic Alkaline Drain Treatment System, a Low Cost Acid Mine Drainage Treatment Alternative. *Proceedings of the National Symposium on Mining*. (University of Kentucky, Lexington, KY). pp. 73-75.

United States Environmental Protection Agency. 1983. *Design Manual: Neutralization of Acid Mine Drainage*. Office of Research and Development, Industrial Environmental Research Laboratory. 231 pp.

Watzlaf, G. R. 1997. Passive Treatment of Acid Mine Drainage in Down-Flow Limestone Systems. *Proceedings of the 1997 National Meeting of the American Society for Surface Mining and Reclamation* (Austin, TX).

Watzlaf, G. R. and R.S. Hedin. 1993. A Method for Predicting the Alkalinity Generated by Anoxic Limestone Drains. *Proceedings of Fourteenth Annual West Virginia Surface Mine Drainage Task Force Symposium* (Morgantown, WV).

Watzlaf, G. R. and D. M. Hyman. 1995. Limitations of Passive Systems for the Treatment of Mine Drainage. *Proceedings of the 17th Annual Association of Abandoned Mine Lands Conference.* (French Lick, IN). p. 186-199.

Watzlaf, G. R., Schroeder, K. T. and C. L. Kairies. 2000. Long-Term Performance of Alkalinity-Producing Passive Systems for the Treatment of Mine Drainage. *Proceedings of the 2000 National Meeting of the American Society for Surface Mining and Reclamation* (Tampa, FL). pp. 262-274.

Watzlaf, G. R., Schroeder, K.T ., and C. L. Kairies. 2001. Modeling of Iron Oxidation in a Passive Treatment System. *Proceedings of the 2001 National Meeting of the American Society for Surface Mining and Reclamation* (Albuquerque, NM). pp. 626-638.

Watzlaf, G. R., Kairies, C. L., and K. T. Schroeder. 2002. Quantitative Results from the Flushing of Four Reducing and Alkalinity-Producing Systems. *Proceedings of the 23rd West Virginia Surface Mine Drainage Task Force Symposium* (Morgantown, WV).

Wieder, R. K. 1989. A Survey of Constructed Wetlands for Acid Coal Mine Drainage Treatment in the Eastern United States. *Wetlands.* 9(2):299-315.

Wieder, R. K. 1994. Diel Changes in Iron (III)/Iron (II) in Effluent from Constructed Acid Mine Drainage Treatment Wetlands. *Journal of Environmental Quality*. 23(4):730-738.

Wieder, R. K. and G. E. Lang. 1982. Modification of Acid Mine Drainage in a Freshwater Wetland. *Proceedings of the Symposium on Wetlands of the Unglaciated Appalachian Region, West Virginia University, Morgantown, WV,* B. R. McDonald, Ed. pp. 43-53.

Wildeman T., Machener, S., Klusman, R., Cohen, R. and P. Lemke. 1990. Metal Removal Efficiencies from Acid Mine Drainage in the Big Five Constructed Wetland. *Proceedings of the 1990 Mining and Reclamation Conference and Exhibition, Vol. II.* pp. 425-433.

Wildeman T. R., Spotts, E., Schafer, W. and J. Gusek. 1994. Characterization, Management and Treatment of Water for Metal-Mining Operations. Short Course at the 1994 Meeting of the American Society for Surface Mining and Reclamation (Pittsburgh, PA), 1994.

Younger, P. L., Banwart, S. A., and R. S. Hedin. 2002. *Mine Water: Hydrology, Pollution, Remediation*. Dordrecht: Kluwer Academic Publishers. 442 pp.

Ziemkiewicz, P. F., J. G. Skousen and J. Simmons. 2003. Long-Term Performance of Passive Acid Mine Drainage Treatment Systems. *Mine Water and the Environment.* 22:118-129.

Exhibit N:

Applications of Passive Treatment to Trace Metals Removal

Applications of Passive Treatment to Trace Metals Removal

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INTRODUCTION

Treatment of wastewater to meet regulatory discharge standards is a significant cost for the electric utility industry, and increasing competition is leading many companies to search for more cost-effective treatment alternatives. One field showing particular promise is *passive treatment technology*, or the design of treatment systems based on processes that cleanse water in the natural environment. These systems generally have much lower operation and maintenance (O&M) costs than conventional chemical treatment and can be successfully applied to a variety of industrial discharges where conditions are favorable to biological and geochemical contaminant removal processes.

A major category of contaminants regulated under the National Pollutant Discharge Elimination System (NPDES) is aqueous metals, also referred to as *trace metals*. One source of metals-bearing wastewater of particular importance to coal-fired utilities is the leachate that can develop from coal combustion by-product (CCB) sites. While generally non-acidic and free of hydrocarbons, CCBs can leach trace metals to water passing through landfills. Parameters that typically exceed compliance limitations are iron and manganese. Depending on local regulations, heavy metals can also be of concern.

To date, Allegheny Power (AP) has installed passive wetland treatment systems to treat metals-bearing leachate at two of its closed CCB facilities. Work was initiated in 1988 with construction of a prototype treatment wetland at the Albright closed CCB landfill in northern West Virginia. With positive results from this system, in 1994 AP entered into a tailored collaboration with the Electric Power Research Institute (EPRI) to advance this cost-saving and environmentally-friendly technology. This jointly-funded project centered on a full-scale application of passive treatment at the Springdale closed CCB landfill in western Pennsylvania and included a major research and development component to evaluate existing and experimental technologies for the treatment of CCB leachate. The research and development team consisted of members from AP, EPRI, the EES Division of Gannett-Fleming, Inc. (EES) and the Pennsylvania State University. This paper has been prepared to summarize the case histories of the Albright and Springdale projects, and to present the findings of the associated research programs with regard to future applications of passive treatment within the utility industry.

HISTORY OF PROJECTS

Albright System

In 1986, the West Virginia Department of Natural Resources (WVDNR) expressed concern that metals-contaminated leachate emanating from the Albright closed CCB landfill was impacting its receiving stream, and indicated that treatment of the discharge would be necessary. Conventional chemical treatment options were evaluated by AP, but were found not to be cost-effective due to the site's remote location, terrain constraints and unmanned status. At the time, passive technology was in its infancy, a promising approach to wastewater compliance, but with no hard design standards applicable to the treatment of CCB leachate. In search of a more cost-effective means of treating these waters, AP retained the services of EES to investigate the viability of using wetland treatment for this site. The investigation and subsequent design led to approval from the WVDNR for construction of an R&D passive wetland treatment system at Albright.

The initial Albright system consisted of four small basins formed by dikes in an existing drainageway and vegetated with transplants from surrounding wetlands. Completed in 1988, this system proved successful in meeting NPDES limitations for iron, but not for manganese. In the early 1990s, work by the US Bureau of Mines (US BoM) indicated that manganese removal rates are much lower than those for iron in wetland environments, and that removal rates for both parameters are largely a function of wetland surface area[1]. Two additional basins were added to the system during 1992 to provide additional surface area and, thereby, increase manganese removal capacity. While showing significant reductions in manganese discharge levels, the expanded system was still unable to meet compliance for that parameter. In 1993, pilot level modifications were made to evaluate preliminary data by others on the ability of limestone beds to remove manganese[2]. Based on these results and findings from the Springdale system after its construction, the Albright system was modified in 1996 to include three rock drains, reaching the final configuration shown by Figure 1. Following a brief period of inoculation for the manganese-oxidizing bacteria, almost total removal was achieved for manganese at Albright, and

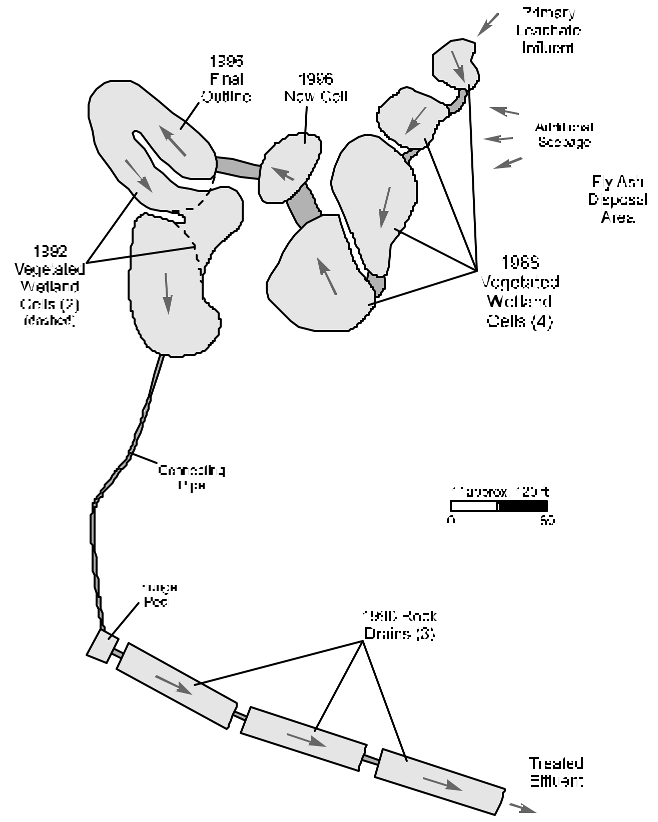

Figure 1. Albright System Layout

that system is now fully in compliance. Each major component of the Albright system has been continually monitored for influent and effluent water quality, and flow, for nearly 10 years.

Springdale System

Leachate from the Springdale landfill underdrain had been discharging since the site was closed in 1975. In 1994, the Pennsylvania Department of Environmental Protection (PADEP) indicated that the existing NPDES permit for this discharge would soon be revised to require more stringent effluent limits on iron and manganese. Based on the success at Albright, AP entered into a Consent Order and Agreement with the PADEP to meet the expanded effluent criteria using passive wetland treatment.

The new NPDES permit also included future compliance with a number of other trace metals for which no passive design standards were available at the time. In response to this need, the AP/EPRI tailored collaboration project was designed with dual purposes of: (1) using proven passive wetland technologies to comply with existing NPDES limits for iron and manganese and (2) designing and evaluating emerging and experimental technologies aimed at achieving eventual compliance with the additional parameters.

At Springdale, insufficient land area was available below the discharge to construct a system to receive gravity flow, necessitating a pumping facility to convey the leachate to a more suitable site uphill. Based on the leachate chemistry, it was determined that compliance with existing dissolved iron limitations could be met by use of a simple oxidation/precipitation basin, which would also equalize the intermittent flow from the pumps before entering a wetland system. These facilities were constructed in 1994 and achieved immediate compliance for dissolved iron. In 1995, eight additional treatment cells were added to the system in advance of issuance of the new NPDES permit. These included four vegetated wetland basins for iron polishing, two rock drains to culture manganese-oxidizing bacteria, an organic upflow cell to promote sulfide mineral formation, and an algal growth basin for vegetative uptake of trace metals. The completed system, shown by Figure 2, was immediately successful in meeting compliance for all parameters except boron, which continues to be the focus of additional efforts by AP to identify an effective passive treatment mechanism.

Influent and effluent loadings were monitored at ten points within the system for a period of two years following construction to evaluate the treatment effectiveness of the major components and technologies for a broad spectrum of parameters. Of particular interest was development of design criteria from the manganese-oxidizing rock drains, which were later applied to achieve manganese compliance at the Albright

Figure 2. Springdale System Layout

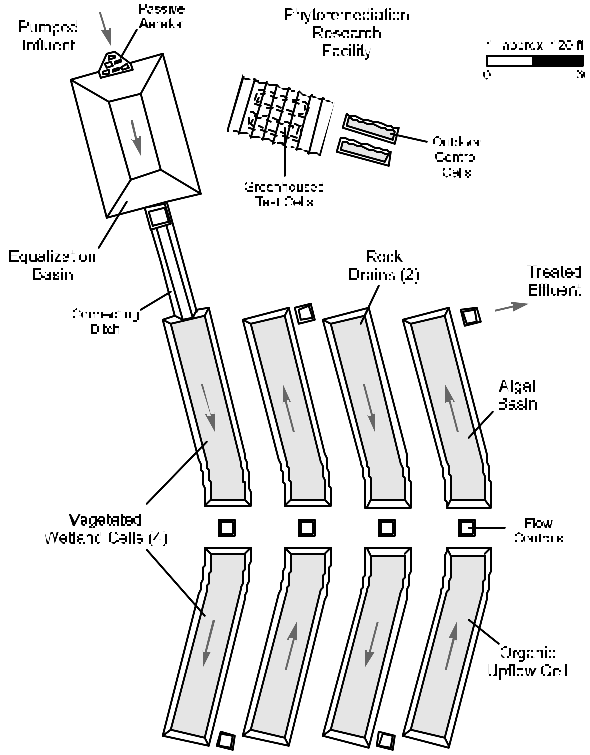

Table 1. Performance Results for Springdale and Albright Passive Treatment Systems

		Albright System			Springdale System		
Parameter		Influent		Effluent	Influent		Effluent
Flow	GPM			20			40
pH	SU	6.50	**15%** †	7.46	7.04	**8%** ‡	7.61
Acid.	mg/L	4	**-79%**	1	23	**-40%** ‡	14
Alk.	mg/L	34	**110%** ‡	72	106	**15%** ‡	121
Al	mg/L	0.628	**-86%**	0.089	0.891	**-71%** ‡	0.260
Sb	mg/L		**			*	
As	mg/L	0.003	**-18%**	0.002	0.061	**-91%** †	0.005
Ba	mg/L		**			*	
Be	mg/L		**		0.0007	**-39%** ‡	0.0004
B	mg/L		**		15.92	**-12%** †	14.03
Cd	mg/L		**			*	
Cr^{3+}	mg/L		**			*	
Cr^{6+}	mg/L		**			*	
Co	mg/L		**			*	
Cu	mg/L	0.001	**51%**	0.002	0.012	**11%**	0.013
Fe, Tot.	mg/L	2.45	**-86%** ‡	0.33	12.46	**-98%** ‡	0.27
Fe, Dis.	mg/L		**		6.09	**-98%** ‡	0.10
Pb	mg/L	0.002	**-19%** ##	0.001		*	
Mn	mg/L	8.52	**-87%**	1.07	2.71	**-92%** ‡	0.21
Hg	mg/L	0.0002	**5%** ##	0.0002		*	
Mo	mg/L		**		0.296	**-38%** ‡	0.183
Ni	mg/L	0.088	**-74%**	0.023	0.063	**-48%** ‡	0.033
Se	mg/L	0.004	**-48%**	0.002	0.002	**-15%**	0.002
Ag	mg/L		**		0.0024	**-85%**	0.0004
Sr	mg/L		**		5.17	**-8%** ‡	4.76
Tl	mg/L		**			*	
Sn	mg/L		**			*	
Ti	mg/L		**			*	
V	mg/L		**			*	
Zn	mg/L	0.083	**-55%**	0.037	0.089	**-72%** ‡	0.024
SO4	mg/L	870	**-17%** ‡	723	1334	**-3%**	1288
SS	mg/L		**		0.2	**-46%** ‡	0.1
TDS	mg/L	1334	**-13%** ‡	1164	1818	**1%**	1828
TSS	mg/L	8	**-87%** ‡	1	25	**-68%** ‡	8

† - Significant at 90%, ‡ - Highly Significant at 95%.
* Non-Detect ** Not Sampled

site. Additional experiments in phytoremediation are continuing in the on-site research facility, which has both greenhouse-enclosed and exposed test cells to evaluate the influence of climate on plant uptake rates.

SELECTED PASSIVE TECHNOLOGIES

The passive technologies employed at Albright and Springdale have proven very effective for removing trace metals. Monitoring results are summarized by Table 1, which shows average influent and effluent parameter concentrations, percent change, and degree of significant. The following provides a brief summary of these technologies and guidelines for their application.

Oxidation/Precipitation Basins

Oxidation/precipitation (O/P) basins are open water impoundments designed to provide aeration for precipitation of aqueous metals, detention time to settle precipitates, and storage volume for accumulating precipitate sludge. They are most effective for removing large-volume sludge formers and are a key component in passive systems where iron is present in quantity. Results from Springdale indicate that arsenic, aluminum, and zinc will also tend to co-precipitate with iron. Iron sludge consists primarily of the amorphous oxyhydroxide *limonite* ($FeOOH \blacklozenge nH_2O$), formed by the process given below. In the aeration step, oxygen is introduced passively by means such as a splash plate or corrugated trough. Limonite sludge forms quickly thereafter, but settles very slowly. A detention time of at least 24 hours is recommended to produce a clear water discharge, with additional storage capacity for accumulated sludge usually maintaining the design detention time at 40% of the total volume occupied.

$$2\,Fe^{2+} + \tfrac{1}{2}\,O_2 + n\,H_2O = FeOOH \blacklozenge nH_2O + 4H^+$$

O/P basins function best in the circumneutral pH range of 6 to 9 SU. A single passive aeration device can only introduce enough oxygen to precipitate about 50 mg/L of iron[3]. For higher loadings, a series of basins and aerators can be employed. Oxidation of aqueous iron results in the generation of acidity (H^+), decreasing the pH of the wastewater. When significant amounts of iron are being removed, measures may be necessary to neutralize excess acidity with downstream components. The rate of iron precipitation also begins to diminish at a pH below 6 SU, with higher concentrations of iron becoming stable despite the presence of oxygen.

Vegetated Wetlands

Vegetated wetlands used for treatment are typically constructed as shallow basins with 1 to 2 feet of organic-rich planting substrate. For optimum plant development, a substrate meeting the classification of clay loam with at least 12% organic content has been found to best duplicate conditions found in natural wetlands[4]. The substrate is planted with species selected as appropriate for the local climate. Cattails are generally the hardiest plants for applications with high metals concentrations or potential for sludge accumulation[5]. Flow within the basins is best regulated at a depth of 0.1 foot or less[6].

Vegetated wetlands function as both physical filters and sites of biogeochemical activity to alter or fix contaminants in place, and are effective against a broad spectrum of parameters. Surface air contact creates an oxygen-rich, *aerobic* environment, which promotes the oxidation and precipitation of aqueous metals. Below the surface, the organic planting substrate consumes oxygen, creating an *anaerobic* environment that promotes sulfide mineral formation. Results from Albright and Springdale show that vegetated wetlands are effective for the removal of aluminum, arsenic, copper, iron, manganese, nickel, and zinc. Other studies indicate vegetated wetlands to be effective against cadmium[7], cobalt[8], and lead[7], and those at Springdale show some effect on beryllium and molybdenum as well. Most other trace metals can be considered candidates for removal in vegetated wetlands, but confirming research is sparse. Boron, commonly associated with CCB leachate, does not show significant removal in vegetated wetlands. Compliance sizing criteria for vegetated wetlands are available from the US BoM[1] for iron, manganese, and acidity based on surface area, as follows:

Iron	10 grams/(meter^2 - day)
Manganese	0.5 grams/(meter^2 - day)
Acidity	3.5 grams/(meter^2 - day)

These values are additive, so a vegetated wetland should be designed with sufficient area to remove each contaminant separately. Preliminary findings from Albright indicate that these criteria may not be sufficient for treatment of iron and manganese to levels approaching 1 mg/L[5]. Vegetated wetlands are limited in their capacity to accommodate large volumes of iron sludge and should be placed after an O/P basin to limit iron loading. Their biological processes will also diminish below a pH of 4 SU. Periodic maintenance is necessary to eliminate flow path short circuits, remove accumulated sludge, and replace spent substrates. Control of internal flow velocities is important for avoiding short-circuits or particle transport. As a general rule, a minimum substrate surface width of 1 foot is recommended for each gallon per minute of influent flow.

Manganese-Oxidizing Rock Drains

"Rock drains" are basins filled with loose stone or gravel that provide substrates for the growth of bacteria which oxidize aqueous manganese (Mn^{2+}) as energy for their life processes. These bacteria combine manganese and oxygen to form the mineral *pyrolusite* (MnO_2), the "black slime" coating commonly found on river rocks. Manganese will not normally precipitate below a pH of 9.5 SU[9] in chemical treatment, but in the presence of bacteria it can be effectively removed in waters with a pH as low as 6 SU and possibly as low as 5 SU[10]. The basic chemical reaction for this can be summarized as follows:

$$Mn^{2+} + H_2O + \tfrac{1}{2}\, O_2 = MnO_2 + 2H^+$$

Detailed design criteria have not been published for rock drains. However, both the Albright and Springdale systems show good performance with basins having a total detention volume of approximately 48 hours. The bacteria grow only on the surface of the stones, so treatment efficiency is believed to also be a function of stone surface area. Rock diameters of 1 to 6 inches appear to produce a good ratio of surface growth area to void space. Water levels within the basins are generally maintained near the surface of the bed, and bacterial growth can occur throughout the water column in the substrate. Multiple basins with intermediate cascade aeration points have been found to introduce the oxygen necessary for the bacterial activity. Manganese-oxidizing bacteria are generally ubiquitous in the environment and will normally colonize a completed rock drain by natural growth within several months of construction.

Rock drains can be very effective against aqueous manganese, showing almost total removal under ideal conditions. They do not appear to function well with an influent iron concentration of greater than 1 mg/L[11], but the Albright application does achieve very low iron and manganese discharge concentrations with an average influent iron of 1.2 mg/L. When treating wastewater containing both iron and manganese, O/P basins and/or vegetated wetlands should be employed to remove iron upstream of a rock drain. At Springdale, the rock drains show some associative reduction of boron, molybdenum, and strontium, while those at Albright show significant reductions in aluminum, arsenic, copper, and nickel at low concentrations.

Organic Reduction Environments

A second bacterially-mediated process with potential for removal of trace metals is sulfate reduction. Anaerobic bacteria decompose organic matter in the presence of sulfates to generate sulfide, a powerful reducing agent. Sulfide is capable of joining with most aqueous metals to form sulfide minerals, with M^{2+} representing the metal in the following:

$$M^{2+} + 4CH_2O + 2SO_4^{2-} =$$
$$MS_2 + H_2 + 2HCO_3^- + 2CO^2 + 2H^2O$$

Organic reduction environments can be created in many forms. One type used for acidity removal is a Sustained Alkalinity Producing System (SAPS), which functions by downflow of water through a layer of compost followed by a layer of limestone. Horizontal migration of water through organic-rich planting substrates will also result in sulfide generation in vegetated wetlands. For the Springdale project, an experimental cell was constructed using upflow through limestone and compost. Although sulfide was produced in abundance by this method, there were insufficient aqueous metals remaining at that point in the system for any significant removal to occur. In fact, some influent metals concentrations were so low that additional amounts were leached from the compost. It is concluded that this method of treatment would be more effective against high concentrations of trace metals, and may not be able to achieve extremely low effluent concentrations.

Phytoremediation

Growing plants must take in nutrients and minerals, including small quantities of trace metals, from their surroundings to produce new tissue. Once incorporated in plant tissue, trace metals tend to be less mobile and are essentially removed from the environment until the plant decays, or possibly longer. A treatment method known as *phytoremediation* uses this basic life process as a tool for removing contaminants from wastewater. Plants do not uptake trace metals as a sufficient percentage of their body mass to make this form of treatment practical for high-concentration parameters, such as iron and manganese. Even if a plant accumulates 1% of its mass in a given metal, that still generates 100 pounds of plant matter for every pound of metal removed. Instead, research is focused on identifying *hyperaccumulators*, those plants that can store exceptionally large amounts of trace metals in their tissues without ill effect. These plants may be a practical treatment method for removing low concentrations of trace metals, and it is suspected that at least some of the trace metal removal occurring at Albright and Springdale is a result of this process.

Research is also focusing on the emerging field of *transmigratory phytoremediation*, where plants modify a contaminant to a benign form and pass it back to the environment, rather than accumulating it in their tissues. This eliminates the potential problem of disposing of large volumes of plant matter. EPRI-supported research is being conducted in conjunction with the Springdale project to examine plant species that can volatilize selenium, continuously removing that contaminant out of wastewater and releasing it to the atmosphere as an innocuous methyl compound[12].

Phased Element Removal Technology

One of the most important developments to come from the AP research has been the recognition that each wastewater contaminant has a preferred environment of removal. Passive systems treating for multiple parameters may require more than one internal treatment method, necessitating some form of ordering protocol. To aid in the design of multi-environment passive systems, EES has developed a set of guidelines known as Phased Element Removal Technology (PERT™)[13], the tenants of which are as follows:

- Generally target contaminants in decreasing order of concentration, as the parameter with the greatest loading often controls the treatment efficiency of lesser constituents.

- Sequence treatment environments in order of increasing sensitivity to chemical or physical loading.

- Eliminate high-volume sludge formers as early as possible in the system and provide sufficient storage volume for the accumulated sludge.

- Use narrow, elongated treatment cells to increase the potential for separation of individual removal processes within multiple-parameter treatment environments.

- Identify limiting reagents and provide mechanisms for their introduction.

- Size components for flow capacity as well as chemical loading capacity to avoid hydraulic overloads and transport of incompatible contaminants to sensitive downstream components.

- Maximize influent contact with the effective treatment substrate through close hydraulic control to prevent flow path short-circuits.

- Allow for ready access to treatment components and for system maintenance, adjustment, and repair.

ECONOMIC ANALYSIS

An extensive cost analysis has been performed for the Springdale passive treatment system[14], and the methodology later applied to the Albright system[5]. Comparisons were made to four chemical treatment alternatives based on capital construction costs and the present values of projected O&M costs. Findings are summarized by Table 2, which compares the results for the two passive systems to the least expensive chemical alternative, a caustic soda drip-feed system, and the most expensive, a hydrated lime silo system. The wastewaters treated at Albright and Springdale are equivalent in chemical loading, and similar construction methods would be required for a chemical alternative on both sites, so this comparison is reasonably accurate.

The Albright system is seen to have a significantly lower capital construction cost than that of the chemical alternatives, while the Springdale system has a comparable cost. The Springdale system includes a number of experimental components that

Table 2. Summary of Estimated Costs for Passive and Chemical Treatment Alternatives

	Passive Treatment		Chemical Treatment	
	Albright System	Springdale System	Low Cost Drip-Feed	High Cost Lime Silo
Capital Construction Cost	$231,965	$701,742	$619,740	$743,980
10 Year O&M Present Value	$115,290	$67,094	$95,344	$148,313
10 Year Total Present Value	**$347,255**	**$768,836**	**$715,084**	**$892,293**

elevate its cost compared to a strictly compliance application. The largest capital cost factor for both forms of treatment is basin construction. The relative requirements for basin construction between passive and chemical alternatives would be approximately equal for other wastewater applications, so similar capital cost performance can be expected on other sites. It is noted that passive systems may require a larger land surface area to construct than chemical alternatives in some cases, and for this reason may not be suited to applications where construction space is severely limited. The opposite can also be true, as the Albright system achieved compliance on a site where a chemical alternative would be extremely difficult to construct. Construction space evaluations and cost estimates should be prepared from conceptual design layouts prior to committing to a given treatment alternative.

In terms of future O&M costs, the Albright system is comparable to the chemical alternatives within a 10 year projection, while the Springdale system is considerably lower. The reduced O&M cost for Springdale reflects less frequent replacement of its treatment substrates, which are protected from sludge accumulation by the equalization basin. Such a basin was not possible in the construction area of the Albright site. Both passive systems have lower operator supervision time, mechanical maintenance, and consumable chemical costs. Passive systems are self-regulating and require only cursory operator supervision, as opposed to chemical systems, which can require frequent or continuous operator presence. Additional savings are realized by eliminating the costs of chemical storage, reporting, and safety training. Longer term projections of O&M costs indicate that both passive systems represent the least expensive alternative as the costs for capital replacement of mechanical chemical system components become a consideration.

CONCLUSIONS

Passive treatment has proven to be a reliable and cost-effective alternative to chemical treatment for the Albright and Springdale CCB sites. Results from both projects have led to significant advances in the understanding of passive removal processes and the development of improved design standards. The technologies employed are readily adaptable to other metals-bearing wastewaters found within the utility industry, provided attention is given to the individual limitations of each treatment method. The cost savings observed for the AP projects are inherent in the nature of passive treatment, and similar savings can be expected for future applications where conditions are appropriate to its use.

As a result of these experiences, passive wetland treatment is now a major component of Allegheny Power's Environmental Management System for CCB facilities.

REFERENCES

1. Hedin, R. S. and Nairn, R. W., "Designing and Sizing Passive Mine Drainage Treatment Systems," Proceedings of Thirteenth Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV, April 8-9, 1992.
2. Eddy, David P., "Treatment of Acid Mine Water Using a Sequential Cell Simulated Wetland: A Mesocosm Experiment," Thesis for The Pennsylvania State University Intercollege Graduate Degree Program, 1994.
3. Hedin, R. S., Nairn, R. W., and Kleinmann, R. L. P., "Passive Treatment of Coal Mine Drainage," Bureau of Mines Information Circular 9389, U.S. BoM, Pittsburgh, PA, 1994.
4. Bishel-Machung, L., Brooks, R. P., Yates, S. S., and Hoover, K. L., "Soil Properties of Reference Wetlands and Wetland Creation Projects in Pennsylvania," Wetlands 16(4): 532-541, 1996.
5. Rightnour, T. A., and Hoover, K. L., "Albright Wetland Treatment System Final Report," AP Internal Document, 1998.
6. Stark, L. R., Brooks, R. P., Webster, H. J., Unz, R. F., and Ulrich, M., "Treatment of Mine Drainage by a Constructed Multi-Cell Wetland: The Corsica Project." Report Number ER9411, Pennsylvania State University, Environmental Resources Research Institute, University Park, PA, 1994.
7. US EPA, "Emerging Technology Summary: Handbook for Constructed Wetlands Receiving Acid Mine Drainage," EPA/540/SR-93/523, 1993.
8. Eger, P., Melchert, G., Antonson, D., and Wagner, J., "The Use of Wetland Treatment to Remove Trace Metals from Mine Drainage," Constructed Wetlands for Water Quality Treatment, Lewis Publishers, Ann Arbor, MI, 1993.
9. Humenick, Michael J., Jr., Water and Wastewater Treatment, Marcel Dekker, Inc., New York, NY, 1977.
10. Gordon, J. A., and Burr, J. L., "Treatment of Manganese from Mining Seep Using Packed Columns," Journal of Environmental Engineering, 115(2): 386-394, 1989.
11. Hedin, R. S., and Nairn, R. W., "Contaminant Removal Capabilities of Wetlands Constructed to Treat Coal Mine Drainage" Constructed Wetlands for Water Quality Improvement, Lewis Publishers, Ann Arbor, MI, p. 187-195, 1993.
12. Zayed, A. and Terry, N., "Selenium Volatilization in Roots and Shoots: Effects of Shoot Removal and Sulfate Level," Journal of Plant Physiology, 143:8-14, 1994.
13. Rightnour, T. A., and Hoover, K. L., "An Application of Phased Element Removal Technology for Passive Treatment of Fly Ash Leachate Contaminants," Environmental Professional Journal, Vol. 19, Special Issue No. 1, 201-208, 1997.
14. Rightnour, T. A., and Hoover, K. L., "An Analysis of Cost Savings for a Constructed Wetland Treatment System," Electric Power Research Institute Interim Report, Draft, July, 1997.

Exhibit O:

Rapid Manganese Removal from Mine Waters Using an Aerated Packed-Bed Bioreactor

Rapid Manganese Removal from Mine Waters Using an Aerated Packed-Bed Bioreactor

Karen L. Johnson* and Paul L. Younger

ABSTRACT

In the UK, the Environmental Quality Standard for manganese has recently been lowered to 30 μg/L (annual average), which is less than the UK Drinking Water Inspectorate's Maximum Permitted Concentration Value (50 μg/L). Current passive treatment systems for manganese removal operate as open-air gravel-bed filters, designed to maximize either influent light and/or dissolved oxygen. This requires large areas of land. A novel enhanced bioremediation treatment system for manganese removal has been developed that consists of a passively aerated subsurface gravel bed. The provision of air at depth and the use of catalytic substrates help overcome the slow kinetics usually associated with manganese oxidation. With a residence time of only 8 h and an influent manganese concentration of approximately 20 mg/L, >95% of the manganese was removed. The treatment system also operates successfully at temperatures as low as 4°C and in total darkness. These observations have positive implications for manganese treatment using this technique in both colder climates and where large areas of land are unavailable. Furthermore, as the operation of this passive treatment system continually generates fresh manganese oxyhydroxide, which is a powerful sorbent for most pollutant metals, it potentially has major ancillary benefits as a removal process for other metals, such as zinc.

MANGANESE IS A COMMON contaminant in many mine waters and though not as ecotoxic as other metals found in such waters (such as Fe, Al, and Zn), it nevertheless has various undesirable properties, including a propensity for precipitating in water distribution pipe networks (eventually causing blockage of supply pipes), imparting an unpleasant "metallic" taste to drinking water, and staining laundry. In the UK, the Environmental Quality Standard (EQS) for manganese has recently been lowered to 30 μg/L dissolved Mn (annual average) to comply with European Directives. This new EQS is actually lower than both the UK Drinking Water Inspectorate's Maximum Permitted Concentration Value and the USEPA's secondary maximum contaminant level, both of which are 50 μg/L in drinking water. For this reason, there has been renewed interest in cost-effective Mn removal technologies.

Manganese is notoriously difficult to remove using either active or passive treatment because of the high activation energy required for Mn oxide precipitation (Crerar and Barnes, 1974). Manganese oxide formation does not readily occur without either highly oxidizing and/or high pH (above pH 9) conditions (Sikora et al., 2000). Manganese oxidation is autocatalytic and is regarded as a two-step process: in the first step, Mn^{2+} is sorbed onto the manganese oxide or oxyhydroxide surface with concomitant partial oxidation of Mn^{2+} to Mn^{3+}; in the second step, the disproportionation of Mn^{3+} to Mn^{4+} occurs (Morgan and Stumm, 1964). The rate of abiotic Mn oxidation has been summarized by Morgan and Stumm (1964), who found it to be dependent on both the concentration of Mn^{2+} ions and the quantity of Mn oxide present (Eq. [1]):

$$\frac{\partial[\mathrm{Mn^{II}}]}{\partial t} = k_0[\mathrm{Mn^{II}}] + k_1[\mathrm{Mn^{II}}][\mathrm{MnO_2}] \qquad [1]$$

where $k_0 = 4 \times 10^{12}\ \mathrm{M^{-3}[O_2{\cdot}Aq][OH^-]^2}$ and $k_1 = 10^{18}\mathrm{[O_2{\cdot}Aq][OH^-]^2}$.

There are numerous strains of bacteria that can increase Mn oxidation rates by as much as five orders of magnitude (Nealson, 1983), the rate being dependent on which species of bacteria is involved (e.g., Zhang et al., 2002). The degree of influence that bacteria have on Mn oxidation has proved difficult to determine, as the majority of metabolic inhibitors that are used to prevent biotic activity in control experiments also influence Mn oxidation rates (Shiller, 2004). Despite these problems, it is widely assumed that Mn oxidation at circumneutral pH is biologically catalyzed (e.g., Zhang et al., 2002).

There are many other catalysts for Mn oxidation, although none are as effective as Mn oxides. Many authors have investigated the catalytic effects of clay minerals on Mn oxidation (Blume and Schwertmann, 1969; Reddy and Perkins, 1976; Wilson, 1980; Yavuz et al., 2003). Reddy and Perkins (1976) found that under alternate wetting and drying conditions, illitic clay was capable of fixing significant quantities of Mn either by physical entrapment or precipitation. Potter and Rossman (1979) proposed that clay minerals (illite and montmorillonite) are necessary for the formation of certain Mn precipitates, such as desert varnish.

Junta and Hochella (1994) characterized the role that mineral surfaces play in the heterogeneous oxidation of Mn^{2+}. They showed that the oxidation of Mn^{2+} begins through adsorption onto "steps" on mineral surfaces. It appears that it is the geometric character, more than the composition, of the immediate surface that plays a significant role in controlling the rate of oxidation during the early stages of the reaction. After the initial oxidation of adsorbed Mn^{2+} at the mineral surface, the newly formed site becomes the most reactive site for continuation of the adsorption–oxidation process.

PASSIVE TREATMENT

Passive treatment utilizes naturally available energy sources such as topographical gradient and microbial metabolic energy

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Abbreviations: SEM, scanning electron microscopy; XRD, X-ray diffraction.

to treat contaminated water and requires regular but infrequent maintenance to operate successfully over its design life (Younger et al., 2002). Because Mn oxidation is difficult in the presence of ferrous iron (Nairn and Hedin, 1993), Mn removal systems are usually placed at the end of the treatment process stream, so that they receive waters from which the majority of the iron has already been removed (Fe < 1 mg/L). Effective Mn removal passive treatment systems are essentially a form of bioremediation, typically consisting of oxic "rock filters," hosting algal and/or bacterial consortia that create high-pH microniches within which the precipitation of Mn oxyhydroxides and oxides occurs (e.g., Phillips et al., 1995; Hamilton et al., 1999). For the algae in such systems to photosynthesize effectively, unobstructed daylight and low influent turbidities are necessary. They are therefore subject to marked seasonal and diurnal variations in performance efficiency.

In the United States, the "Pyrolusite Process" (Vail and Riley, 2000), a patented bioremediation method, has been successfully used to treat manganiferous waters. In this system, a limestone gravel reactor is inoculated with manganese-oxidizing bacteria, which are chosen site specifically. However, recent work (Rose et al., 2003) suggests that special inoculation may not be necessary.

All of these existing systems require relatively large areas of land as they must be shallow to ensure sufficient infiltration of light and/or dissolved oxygen. The new enhanced bioremediation method discussed in this paper takes the form of a subsurface flow gravel bed (Johnson, 2003a). The provision of air at depth is achieved using a passive aeration system and the use of a catalytic substrate helps overcome the slow kinetics that are usually associated with Mn oxidation and, most importantly, allows deeper systems to be built where large areas of land are not available.

MATERIALS AND METHODS

Static batch experiments (250 mL) were performed to identify suitable substrates and conditions for Mn removal. The results (Johnson, 2003b) directed us toward a dolomite substrate with a bentonite and MnO_2 (Sigma-Aldrich, St. Louis, MO) basal layer, as this combination proved to be the most effective at promoting Mn oxidation.

Experimental Design

Continuous flow experiments were set up and operated at room temperature and in natural light conditions (unless otherwise stated) for a total of 277 d. The design of each reactor consisted of a 5-L rectangular plastic container with an influent pipe near the bottom and an effluent pipe near the top on the opposite side (Fig. 1). This arrangement of flow was designed to limit the development of preferential flow-paths.

Three containers (A, B, and C) were filled to a depth of 1 cm with bentonite, which was saturated with deionized water. A 1-mm layer of MnO_2 powder was added to the hydrated bentonite surface. Finally the container was filled with clean single-size 20-mm-diameter dolomite clasts from the Raisby quarry (Raisby formation) in northeastern England (UK National Grid Reference NZ 311 337). A fourth reactor was set up as a "control," containing only relatively inert quartzite gravel in place of the dolomite and MnO_2 powder (though still with bentonite as in the other reactors). Mine water was pumped into and out of the system using two separate peristaltic pumps. Aeration of the substrate was provided using an aeration pump. In the field, aeration of the substrate would be provided using a passive aeration system that uses modest heads of water to produce blasts of compressed air.

A key part of this work was to understand the role of aeration in enhancing Mn oxidation at various stages of biofilm development and under different environmental conditions. Dissolved oxygen levels in the influent and effluent water were measured on a weekly basis using a YSI (Yellow Springs, OH) Model 95 meter, which was calibrated using air as a standard for 100% dissolved oxygen. However, dissolved oxygen in the bioreactors themselves was not monitored. Reported dissolved oxygen concentrations are accurate to ±2%. The pH was measured on a weekly basis using a Camlab (Cambridge, UK) MY/6P Ultrameter. Readings are accurate to ±0.01 pH unit.

The reactors were operated with and without aeration both at room temperature and at 4°C at different stages of biofilm development. It should be noted that the quartzite reactor was not operated without aeration during the start-up phase or operated at 4°C due to the fact that only one control reactor could be accommodated. When the dolomite reactor was operated at 4°C, the light was left switched on in the cold room to distinguish between temperature and light effects and subsequently (once it was demonstrated that light was not a controlling factor in the manganese removal process) the reactor was operated in complete darkness for the remaining period.

Substrate and Mine Water Characterization

Net-alkaline mine water from a recently closed (December 1998) fluorite mine (Frazer's Grove Mine in the North Pennines, United Kingdom; Johnson and Younger, 2002) was used in the laboratory experiments. The authors felt it was important to use real mine water as it is preferable to use in situ

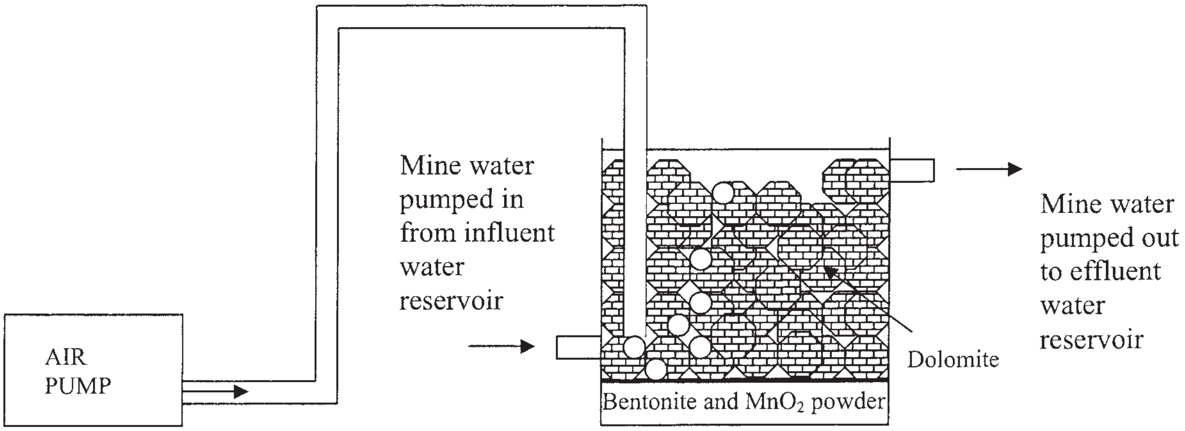

Fig. 1. Sketch diagram (not to scale) of the small-scale continuous flow experiments.

microbial communities (Johnson, 2003), which are more representative of real ecosystems than synthetic systems. The water had a pH of 7. The geochemistry of the mine water varied with time due to ground water rebound in the area of the mine [see Johnson and Younger (2002) for more detailed geochemical analysis]. During the experimental period, we measured bicarbonate alkalinity values between 120 to 160 mg/L as $CaCO_3$ equivalent, and 15 to 30 mg/L Mn, 5 to 10 mg/L Fe, and 5 to 10 mg/L Zn. The water was stored for 72 h before use to allow the iron to precipitate out to ensure that ferrous iron could not interfere with the Mn oxidation process. Metal concentrations were measured after this storage period using a Unicam (Cambridge, UK) 929 atomic absorption spectrophotometer. Analytical precision was ±0.1 mg/L. Effluent water samples were taken from the reactors on a daily basis, filtered (using 0.45-μm filters), and acidified. There was no significant difference in metal concentrations between filtered and nonfiltered samples except for samples taken from the control reactor during the period of reaeration.

Flow rates were measured using a graduated container and stop-watch, and nominal residence times were calculated accordingly, taking into account the porosity of the bentonite and dolomite system (determined to be approximately 50%). Flows were generally adjusted to ensure a residence time of around 8 h (approximately 5 mL/min flow rate) as the initial batch experiments had indicated that the majority of Mn and Zn would be removed in this time (Johnson, unpublished data). All percentage removals quoted for Mn and Zn are for an 8-h residence time.

No microbiological analyses were performed on the substrates or the water due to resource limitations at the time the work took place. However, Reactor B was poisoned (using the disinfectant Virkon [DuPont, Wilmington, DE]) on Day 148 to gain some understanding of the degree of abiotic versus abiotic manganese oxidation. At the end of the experimental period, biofilm-covered dolomite clasts were removed from Reactor C and compared with fresh dolomite using X-ray diffraction (XRD), scanning electron microscopy (SEM), and elemental analysis.

RESULTS

Dissolved oxygen levels in both the influent and effluent waters were always >95% (±2%); this is likely to be due to the fact that both influent and effluent vessels were open to the atmosphere. Effluent pH was between 8.00 and 8.20 in all reactors for the duration of the experimental period.

The results for the aerated dolomite and quartzite reactors can be categorized into two phases: an initial "start-up" period lasting approximately 2 mo, during which 60% of the influent Mn and 85% of the influent Zn were removed in the dolomite reactors and 40% of the influent Mn and 83% of the influent Zn were removed in the quartzite reactor; and a second "established" part of the experiment, when a black biofilm became evident on the substrate surfaces, during which 97% of the influent Mn and 93% of the influent Zn were removed in the dolomite reactors and 90% of the influent Mn and 90% of the influent Zn were removed in the quartzite reactor.

The addition of the disinfectant Virkon to Reactor B on Day 148 resulted in the breakdown of the black manganese oxyhydroxide biofilm, which was partly washed away. The effluent remained acidic and effervescent for several weeks afterward. Percentage Mn removal decreased to approximately 29% and percentage Zn removal to approximately 66% after the disinfectant had been added. There was no change in either Mn or Zn percentage removal with or without aeration.

Figure 2 shows the effect of aeration on Mn removal in the dolomite reactors during the start-up phase. When aeration was removed from Reactor B, effluent Mn concentration increased and the reactor subsequently took longer to become "established." It is interesting to note that the nature of the start-up phase is very different in the dolomite and quartzite reactors. The dolomite

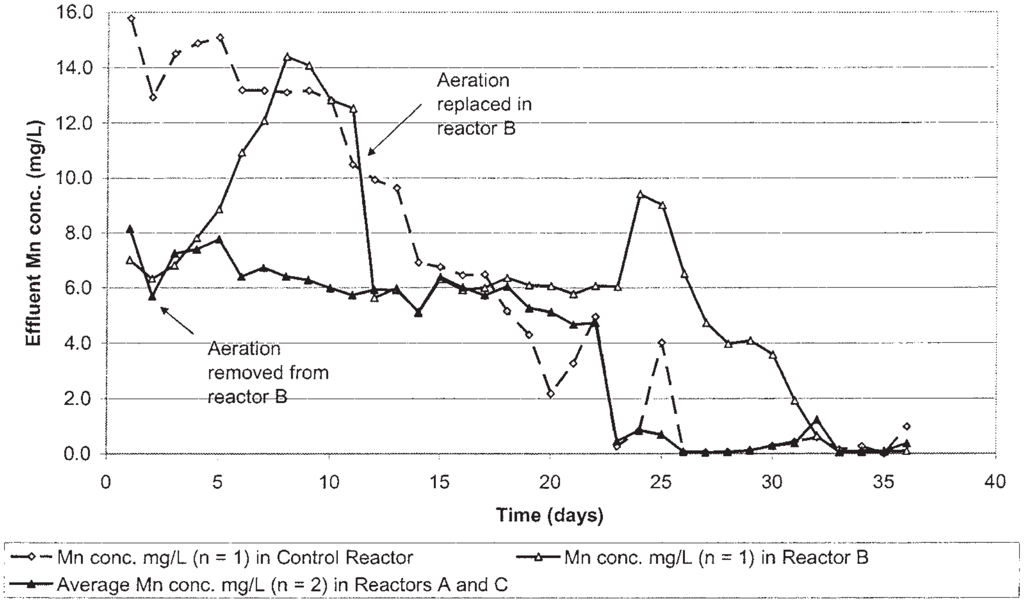

Fig. 2. Effluent manganese concentration in the quartzite (control) and dolomite reactors (Reactor B and average of Reactors A and C) showing the effect of aeration during the start-up phase.

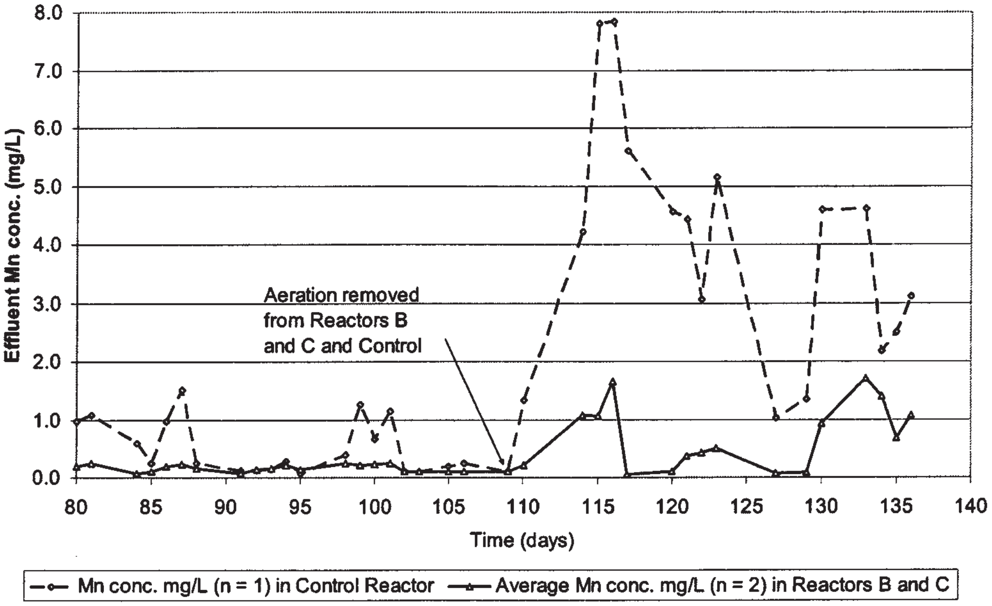

Fig. 3. Effluent manganese concentration in the quartzite (control) and dolomite reactors (average of Reactors B and C) showing the effect of aeration during the established phase.

reactors all removed approximately 60% of influent Mn during the start-up phase and there was a step increase to approximately 97% Mn removal during the established phase. In comparison, Mn removal in the quartzite reactor increased gradually during the start-up phase until it reached approximately 90% removal in the established phase.

Figure 3 shows the effect of aeration on Mn removal in the dolomite and quartzite reactors during the established phase. When aeration was removed from the dolomite (B and C) and the quartzite (control) reactors, effluent Mn concentration increased more in the quartzite reactor than in the dolomite reactors. The difference in Mn removal performance between the dolomite and quartzite reactors is most clear during the reintroduction of aeration. Figure 4 shows that when aeration was reintroduced, Mn effluent concentrations returned to previous (aerated) levels in the dolomite reactor whereas they did not return to previous (aerated) levels in the quartzite reactor. It was also noted that Mn oxyhydroxide deposits were dislodged during the reaeration process in the quartzite reactor whereas the attachment was undisturbed in the dolomite reactors.

Figure 5 shows both Mn and Zn removal performance in the dolomite reactor (A) at 4°C. It is clear that Mn and Zn removal is inhibited at 4°C without aeration. There is no explanation for the precipitous drop in effluent Mn concentrations around Day 100 but it does dem-

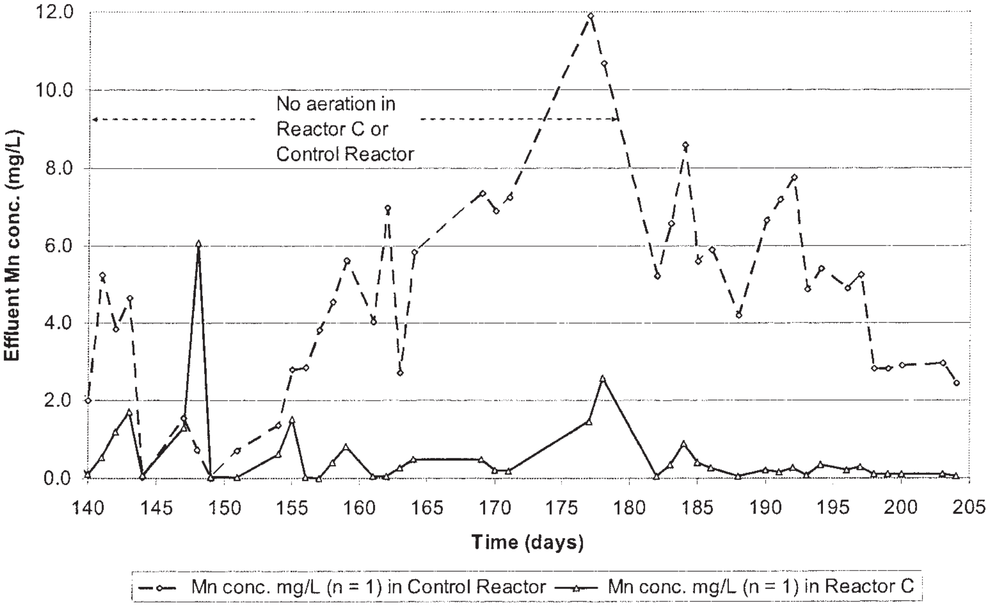

Fig. 4. Effluent manganese concentration in the quartzite (control) and dolomite reactor (Reactor C) showing the effect of the reintroduction of aeration in the established phase.

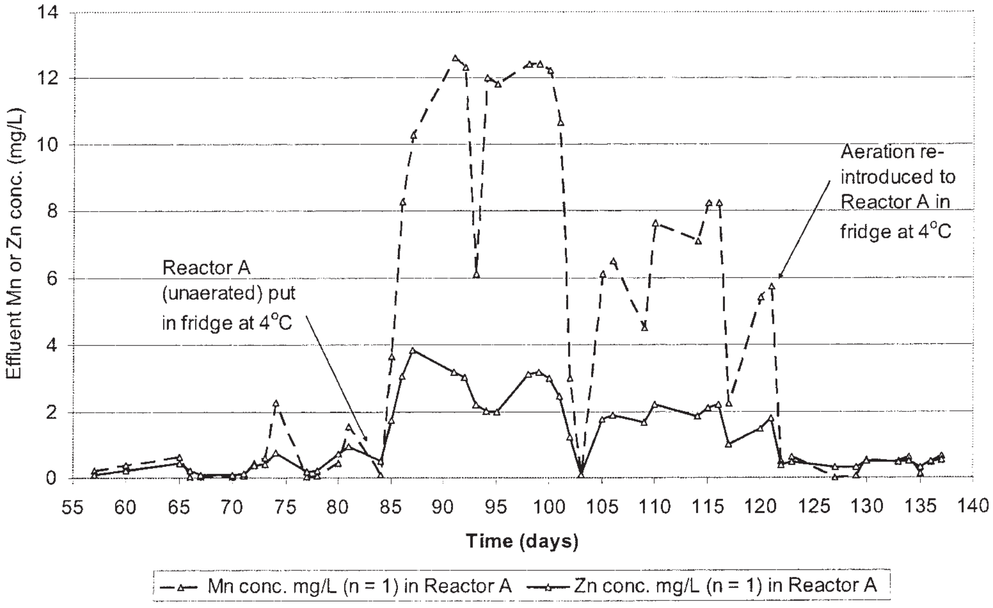

Fig. 5. Effluent manganese and zinc concentrations in the dolomite reactor (Reactor A) showing the effect of aeration during operation at 4°C.

onstrate the large variability in the data. With aeration, at 4°C, Mn and Zn removal returned to previous (unaerated at 20°C) levels. When aeration was moved from the substrate (as is shown in Fig. 1) to the influent water reservoir there was a decrease in Mn removal equivalent to there being no aeration (data not shown on graph).

Figure 6A shows that there were some Mn deposits present on the surface of the dolomite before its use in the reactors. It is clear from Fig. 6B that after use in the reactors the Mn deposit is quite extensive in its coverage. The XRD peak count was very low due to the largely amorphous nature of the deposit but four of the five greatest peaks characteristic of nsutite (γMnOOH) were present in the diffractogram (d-spacings: 4.00_x, 1.64_x, 2.42_7, and 2.13_5) and it is likely that this is the only crystalline phase present.

Elemental analysis suggests that the black precipitate is an oxide with a Mn to Zn relative abundance ratio of 3:1, which is consistent with the molar ratios of Mn to Zn removed in the continuous flow experiments. There were also significant quantities of calcium present in the precipitate although it is not clear whether the Ca is part of the black precipitate or if we are "seeing" the Ca from the dolomite underneath. However, Tipping et al. (1984) found Ca to be abundant in the Mn oxyhydroxides precipitated from natural lake waters in northwestern England. Aluminium and silica are also present in the analysis of the black deposit suggesting that a clay mineral (possibly bentonite) may be associated with the black deposit.

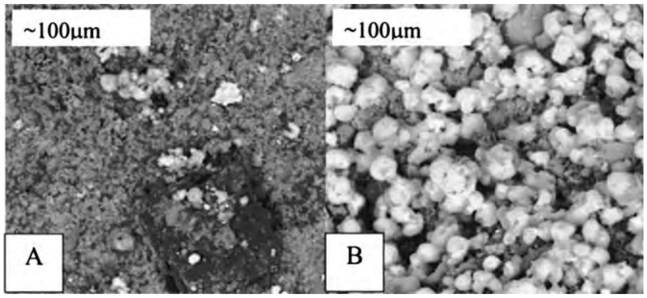

Fig. 6. Secondary electron image of the dolomite both before (A) and after (B) use in the continuous flow experiments showing Mn deposit (light areas) on the dolomite (dark areas). The scale bar shows 100 µm.

DISCUSSION

All of the reactors took approximately 8 wk to become "established." This appears to be a common "start-up" period for microbial communities engaged in Fe and Mn oxidation (Bourgine et al., 1994). The percent metal removed was greater during the established phase than during the start-up phase in both the dolomite and the quartzite reactors. The start of the established phase coincided with the development of a black precipitate (biofilm) on the substrate surface. Although no attempt was made to identify the species of manganese-oxidizing bacteria present, the addition of the disinfectant Virkon resulted in a dramatic decrease in percentage Mn and Zn removed. The decrease to approximately 29% Mn removal after the addition of disinfectant may give an indication of the amount of manganese removal that was taking place without microorganisms. However, the facts that dead cells may still provide more sorption sites than the inorganic substrate alone and the lower pH environment created by the addition of Virkon may have affected the percentage Mn removed. Therefore, 29% may not be an accurate estimate of abiotic percentage Mn removed but it does indicate that Mn removal was at least in part a biotic process. It is interesting to note that in the acidic environment, Zn removal is relatively higher than Mn removal in comparison with percentage removals under circumneutral conditions. This may be due to preferential adsorption of Zn over Mn onto manganese oxyhydroxides at low pH (whereas at circumneutral pH Mn is preferentially adsorbed) (Nicholson and Eley, 1997).

The black precipitate recovered from the surface of the dolomite was nsutite, γMnOOH, which was identified using XRD. The smaller peaks for nsutite were not present but this is likely to be due to the amorphous nature of much of the precipitate; Giovanoli (1980) specifically points out the difficulty in definitively identifying nsutite using XRD. Elemental analysis using SEM showed that there was Zn present, presumably as a sorbed phase, on the surface of the nsutite. The relative abundance of Mn to Zn of was 3:1, which was also the approximate molar ratio of Mn to Zn in the influent water for the majority of the time. There is a positive correlation ($R^2 = 0.74$) between percent Mn removed and percent Zn removed in the dolomite reactors. However, there is a statistically insignificant relationship ($R^2 = 0.20$) between the Mn and Zn removed in the quartzite reactor. This is probably due to the greater variability in both Mn and Zn removal in the quartzite reactor.

During the start-up phase (with aeration), approximately 40 and 60% of Mn were removed in the quartzite and dolomite reactors, respectively. During the established phase (with aeration), the difference between the two types of reactor was less noticeable with approximately 90 and 97% of Mn removed in the quartzite and dolomite reactors, respectively. However, the variation in percent Mn removed in both the start-up and the established phases was greater in the quartzite reactor than in the dolomite reactors, suggesting that the dolomite/MnO_2 combination provides a better substrate surface for sustaining high percentage manganese removal.

The effects of aeration were examined during both the start-up and established phases in the dolomite reactor and it is clear that aeration is important at both stages. The dolomite reactors removed approximately 60% of the influent Mn in the start-up phase with aeration compared to approximately 22% without aeration. During the established phase, the difference was less noticeable in the dolomite reactor with approximately 97% of Mn removed with aeration and approximately 91% Mn removed without aeration. The quartzite gravel reactor was more dependent on aeration to sustain high percentage Mn removal. In the established phase, approximately 90% of the Mn was removed with aeration in the quartzite gravel reactor, dropping to approximately 60% Mn removal without aeration. This suggests that during the established phase, maintaining high percentage manganese removal in the dolomite reactor was less dependent on aeration than the quartzite reactor.

The differences in Mn removal performance between the quartzite and dolomite reactors are also noticeable during the reaeration phase. With the reintroduction of aeration, the quartzite reactor only recovers to approximately 67% Mn removal whereas the dolomite reactors recover completely to approximately 97% Mn removal. It was noted that the black precipitate that had coated the quartzite gravel was significantly dislodged by the reintroduction of aeration, whereas the precipitate on the dolomite substrate remained attached during the second phase of aeration. This suggests that the dolomite substrate provides a better surface for the attachment of Mn oxyhydroxide precipitates than the quartzite gravel. The reasons for the superiority of the dolomite surface over the quartzite surface could be due to the physical characteristics of the substrates such as surface roughness (SEM photographs of the dolomite and quartzite surfaces show that the dolomite surface is much rougher than the quartzite surface; Johnson 2003b) or geochemical properties. The authors have started a new research project to address this question and are currently running bioreactors in triplicate using the pure minerals calcite, dolomite, magnesite, and quartzite. In this work, environmental scanning electron microscopy (E-SEM) will be used to assess the spatial distribution and composition of the manganese removing biofilms and the associated manganese oxyhydroxides that accumulated on the substrate surface. Biofilm community development and composition will be monitored over time using denaturing gradient gel electrophoresis (DGGE). Pilot-scale reactors have also been established in the field at three different sites in northeastern England.

Since approximately 0.15 to 0.30 mg/L of dissolved oxygen are required to oxidize 1 mg/L Mn^{2+}, either partially to Mn^{3+} or fully to Mn^{4+} (Sikora et al., 2000), there is more than sufficient oxygen present in fully saturated waters (which typically contain approximately 10 mg/L dissolved oxygen) to oxidize the approximately 20 mg/L of dissolved Mn^{2+} in the influent water. Since we know that the influent water was nearly saturated in dissolved oxygen, this suggests that it was not the extra oxygen provided by the aeration that increased Mn removal but the actual aeration process. This hypothesis is supported by the fact that when the influent water reservoir was aerated directly (rather than as shown in Fig. 1) while the reactor was in the cold room, there was a subsequent decrease in percentage Mn removed equivalent to no aeration being present. The generation of bubbles at the substrate surface probably increased the potential mass transfer of oxygen (Baylar and Emiroglu, 2004) to the reactive surfaces, thereby making oxygen more readily available to take part in the oxidation process and support other essential microbiological support systems. The importance of this aeration was highlighted when the reactors were exposed to stressful environmental conditions such as low temperatures. Without aeration, Mn removal in the dolomite reactor fell dramatically from approximately 97% to approximately 38%. When the reactor was reaerated, manganese removal increased back to approximately 97% within 24 h. It seems plausible that the group of microorganisms that were successfully aiding Mn removal without aeration at room temperature were not able to continue doing so at 4°C; with their subsequent drop in activity and the reintroduction of aeration, another group of microorganisms were able to take advantage of the environment and enhance Mn removal once again.

Metal removal rates quoted for wetland-type passive treatment systems are usually quoted in units of $g/m^2/d$ (e.g., Hedin et al., 1994), where the m^2 term refers to land area. This allows one to compare the land requirements of various treatment options. However, this is clearly not appropriate for a volume-based treatment system. Calculations were performed to determine the amount of Mn removed in the small-scale continuous flow experiments both in g/m^3/d and in g/m^2/d (assuming a subsurface treatment system depth of 1 m). With an 8-h residence time, the Mn removal rate was calculated as 60 g/m^2/d, which is an order of magnitude greater than those quoted by Nairn and Hedin (1993) and demonstrates the ability of the treatment system to overcome the slow oxidation kinetics usually associated with Mn oxidation. This has major implications for the treatment of manganiferous waters in areas where there is little land available. Furthermore, as the operation of this passive treatment system continually generates fresh Mn oxyhydroxide, which is a powerful sorbent for most pollutant metals (Jenne, 1968), it potentially has major ancillary benefits as a removal process for other metals such as zinc.

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REFERENCES

Baylar, A., and M.E. Emiroglu. 2004. An experimental study of air entrainment and oxygen transfer at a water jet from a nozzle with air holes. Water Environ. Res. 76(3):231–237.

Blume, H.P., and U. Schwertmann. 1969. Genetic evaluation of profile distribution of Al, Fe and Mn oxides. Soil Sci. Soc. Am. Proc. 33:438–444.

Bourgine, F.P., M. Gennery, J.I. Chapman, H. Kerai, J.G. Green, R.J. Rap, S. Ellis, C. Gaumard, C. Stretton, J. Chandler, K. Kaur, C. Harwood, A.A. Redhead, P. Howsam, J. Beechey, D. Osbourne, and B. Giles. 1994. Biological processes at Saints Hill water-treatment plant, Kent—Discussion. J. Inst. Water Environ. Manage. 8(4):379–392.

Crerar, D.A., and H.L. Barnes. 1974. Deposition of deep-sea manganese nodules. Geochim. Cosmochim. Acta 38:270–300.

Giovanoli, R. 1980. On natural and synthetic manganese nodules. p. 159–202. *In* I.M. Varentsov (ed.) Geology and geochemistry of manganese. 2nd Int. Symp., Sydney, Australia. Akademiai Kiado, Stuttgart, Germany.

Hamilton, Q.U.I., H.M. Lamb, C. Hallett, and J.A. Proctor. 1999. Passive treatment systems for the remediation of acid mine drainage at Wheal Jane, Cornwall. Water Environ. Manage. 13:93–103.

Hedin, R.S., R.W. Nairn, and R.L.P. Kleinmann. 1994. Passive treatment of polluted coal mine drainage. Bureau of Mines Info. Circ. 9389. United States Dep. of Interior, Washington, DC.

Jenne, E.A. 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. p. 337–387. *In* Trace inorganics in water. Advanced Chemistry Series 73. Am. Chem. Soc., Washington, DC.

Johnson, D.B. 2003. Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines. Water Air Soil Pollut. 3:47–66.

Johnson, K.L. 2003a. The importance of aeration in passive treatment schemes for manganese removal. Land Contamination Reclamation 11(2):205–212.

Johnson, K.L. 2003b. Oxidative passive treatment to remove Mn^{2+} from mine waters: What is the best substrate? p. 85–97. *In* 8th Int. Mine Water Association Congress, Johannesburg, South Africa. IMWA, Johannesburg.

Johnson, K.L., and P.L. Younger. 2002. Hydrogeological and geochemical consequences of the abandonment of Frazer's Grove carbonate hosted Pb/Zn fluorspar mine, North Pennines, UK. p. 347–364. *In* P.L. Younger and N.S. Robins (ed.) Mine water hydrogeology and geochemistry. Spec. Publ. 198. Geol. Soc., London.

Junta, J.L., and M.F. Hochella. 1994. Manganese (II) oxidation at mineral surfaces: A microscopic and spectroscopic study. Geochim. Cosmochim. Acta 58:4985–4999.

Morgan, J.J., and W. Stumm. 1964. Colloid-chemical properties of manganese dioxide. J. Colloid Sci. 19:347–359.

Nairn, B., and R.S. Hedin. 1993. Contaminant removal capabilities of wetlands constructed to treat coal mine drainage. p. 187–195. *In* G.A. Moshiri (ed.) Constructed wetlands for water quality improvement. Lewis Publ., Boca Raton, FL.

Nealson, K.H. 1983. The microbial manganese cycle. *In* W.E. Krumbein (ed.) Microbial geochemistry. Blackwell Sci. Publ., Oxford.

Nicholson, K., and M. Eley. 1997. Geochemistry of manganese oxides: Metal adsorption in freshwater and marine environments. p. 309–326. *In* K. Nicholson, J.R. Hein, B. Buhn, and S. Dasgupta (ed.) Manganese mineralisation: Geochemistry and mineralogy of terrestrial and marine deposits. Spec. Publ. 119. Geol. Soc., London.

Phillips, P., J. Bender, R. Simms, S. Rodriguez-Eaton, and C. Britt. 1995. Manganese removal from acid coal-mine drainage by a pond containing green algae and microbial mat. Water Sci. Technol. 31(12):161–170.

Potter, R.M., and G.R. Rossman. 1979. Mineralogy of manganese dendrites and coatings. Am. Mineral. 64:1219–1226.

Reddy, M.R., and H.F. Perkins. 1976. Fixation of manganese by clay minerals. Soil Sci. 121:21–24.

Rose, A.W., P.J. Shah, and B. Means. 2003. Case studies of limestone-bed passive systems for manganese removal from acid mine drainage. p. 1059–1078. *In* Proc. of the 20th Conf. for the American Society of Mining and Reclamation, Billings, MT. ASMR, Lexington, KY.

Shiller, A.M. 2004. Temperature dependence of microbial Mn oxidation as a control on seasonal concentration variability of dissolved metals in flood-plain rivers. *In* Proc. of the 227th National American Chemical Society Spring Meeting, Anaheim, CA. 28 Mar.–1 Apr. 2004 [Online]. Available at http://membership.acs.org/g/geoc/Anaheim_2004_Abstracts.pdf (verified 31 Jan. 2005). Am. Chem. Soc., Washington, DC.

Sikora, F.J., L.L. Behrends, G.A. Brodie, and H.N. Taylor. 2000. Design criteria and required chemistry for removing manganese in acid mine drainage using subsurface flow wetlands. Water Environ. Res. 72(5):536–544.

Tipping, E., D.W. Thompson, and W. Davison. 1984. Oxidation products of Mn(II) in lake waters. Chem. Geol. 44:359–383.

Vail, W.J., and R.K. Riley. 2000. The Pyrolusite Process: A bioremediation process for the abatements of acid mine drainage. Green Lands 30(4):40–46.

Wilson, D.E. 1980. Surface and complexation effects on the rate of Mn (II) oxidation in natural waters. Geochim. Cosmochim. Acta 44:1311–1317.

Yavuz, O., Y. Altunkaynak, and F. Guzel. 2003. Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. Water Res. 37:948–952.

Younger, P.L., S.A. Banwart, and R.S. Hedin. 2002. Mine water: Hydrology, pollution, remediation. Kluwer, Amsterdam.

Zhang, J., L.W. Lion, Y.M. Nelson, M.L. Shuler, and W.C. Ghiorse. 2002. Kinetics of Mn(II) oxidation by Leptothrix discophora SS1. Geochim. Cosmochim. Acta 65(5):773–781.