

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.

Acknowledgements

The authors would like to thank the technical reviewers whose comments were greatly appreciated: Arthur W. Rose, Paul L. Younger, Carl S. Kirby and Ben B. Faulkner. Laboratory analyses were conducted by Mark Wesolowski, Joyce Swank, Dennis Viscusi, Harry Williams, Hubert McDonald and Lillian Schlosser Balchus. John Kleinhenz, Randy Woods and John Odoski assisted with field sampling and monitoring. We are indebted to the following individuals who shared information on the construction of many of the passive treatment systems discussed in this report: Doug Kepler, Eric McCleary, Dan Seibert, Margaret Dunn, Tim Danehy, Connie Lyons and Joe Mills.

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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, Na₂CO₃, or NH₃) 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 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 recurvum* 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

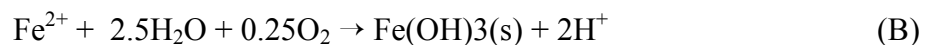
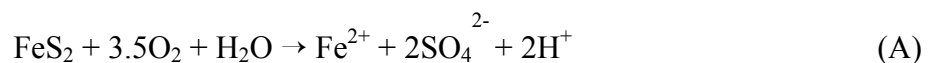
systems. However, failures can be very damaging to the perceived effectiveness of the technology. In general, we have found that the systems that were not effective or failed were undersized, improperly designed, or both. The key is to understand the limitations of each unit's operation, to have reasonable 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 (FeS₂). 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):

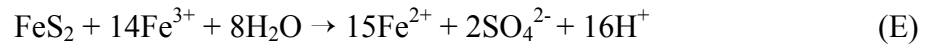
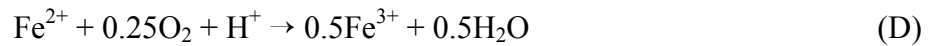


Iron-oxidizing bacteria accelerate pyrite oxidation by two mechanisms: direct oxidation, and oxidizing Fe²⁺ to Fe³⁺, which in turn oxidizes the sulfide minerals (Beck and Brown, 1968, Duncan et al. 1967, Groudev 1979, Silverman 1967). Direct oxidation is probably most important during initial acidification, when complete hydrolysis of Fe³⁺ 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 Fe²⁺ slows down dramatically, according to the rate law:

$$\frac{-d(\text{Fe}^{2+})}{dt} = k \frac{(\text{O}_2(\text{aq}))(\text{Fe}^{2+})}{(\text{H}^+)^2} \quad (\text{C})$$

where (Fe^{2+}) , $(\text{O}_2(\text{aq}))$, 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):



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 $\text{Fe}(\text{OH})_3$ 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, but circumneutral 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.)

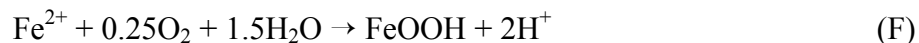
Aluminum generally hydrolyzes and precipitates as Al(OH)₃, which is a white particulate. Other aluminum compounds with silica and sulfate can also form, depending on the environmental conditions. Oxidation is not required, and apparently bacterial activity is not a factor. Precipitation of aluminum requires 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 MnO₂, 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 CO₂-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⁺.





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,

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

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):

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

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.

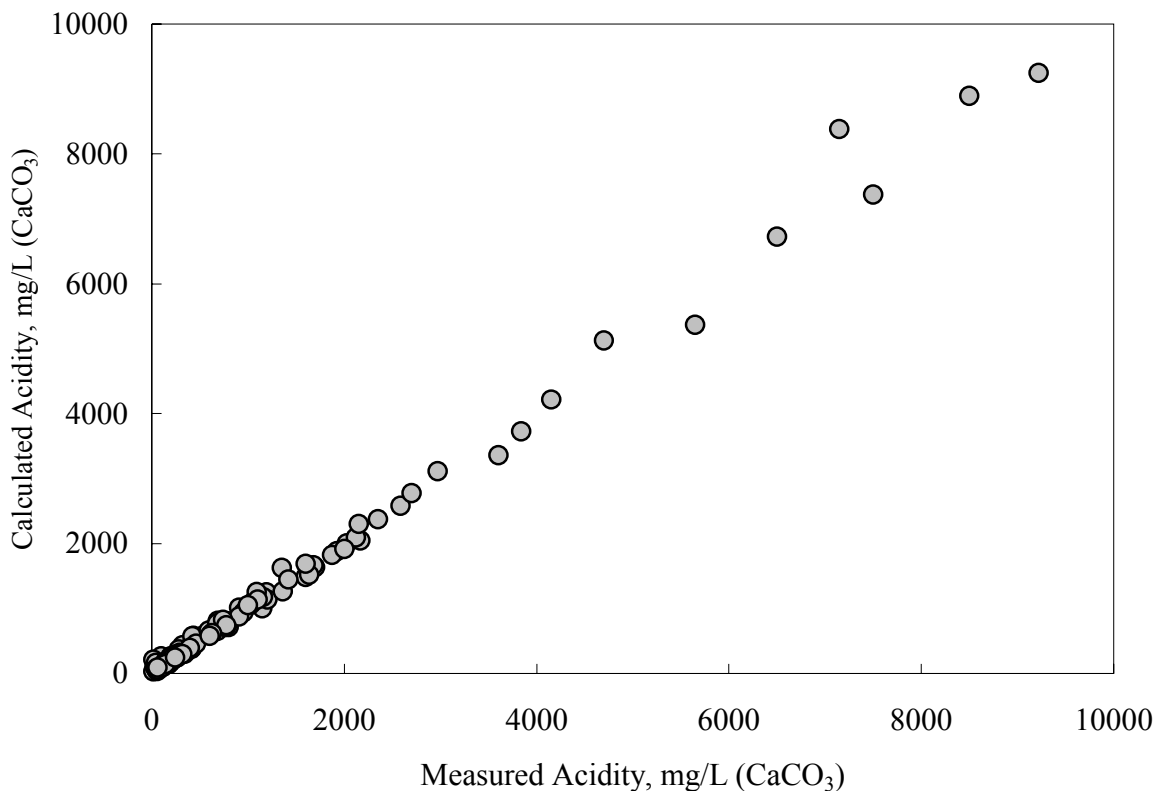


Figure 1. Calculated Versus Measured Acidity for Over 150 Coal Mine Discharges

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
Fe²⁺	225	402	88	60	107	31	<1	<1	<1	55	98	93
Fe³⁺	<1	<1	<1	4	11	3	20	54	20	<1	<1	<1
Al³⁺	<1	<1	<1	30	167	48	18	100	37	<1	<1	<1
Mn²⁺	29	53	12	22	40	12	13	24	9	4	7	7

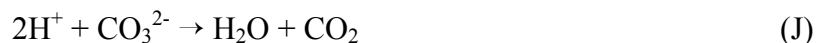
pH in standard units. Fe²⁺, Fe³⁺, Al³⁺ and Mn²⁺ concentrations in mg/L. A.C. is acidity contribution in mg/L as CaCO₃.

Table 3. Proton Acidity Contributions at Various pH Values

pH	Acidity Equivalent (mg/L as CaCO₃)
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 (HCO₃⁻) or carbonate (CO₃²⁻) 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).





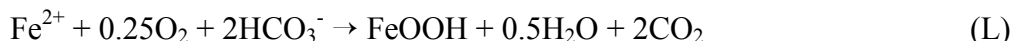
The presence of bicarbonate alkalinity in mine waters with elevated levels of metals is not unusual, particularly in anoxic waters. Table 4 shows the chemical composition of six mine waters in northern Appalachia that contain alkalinity, and are also contaminated with ferrous iron and manganese. None 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 CaCO₃, 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 Fe²⁺, the net reaction for the oxidation, hydrolysis and neutralization reactions is:



Reaction L indicates that net alkaline waters contain at least 1.8 mg/L alkalinity for each 1.0 mg/L of dissolved Fe²⁺. 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 Fe²⁺, 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 CaCO₃. 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 CaCO₃/L” and “the alkalinity to pH ___ = ___ mg as CaCO₃/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 CaCO₃), 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 CaCO₃), as being net alkaline (50 mg/L as CaCO₃).

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 asCaCO₃ and alkalinity as 105 mg/L as CaCO₃. For water B, they would list acidity as 150 mg/L and alkalinity as 100 mg/L as CaCO₃. 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

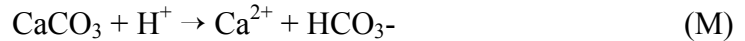
Parameter	Times Reported	Mean	Median	Minimum	Maximum
Flow	54	601	71.5	5.50	15600
pH	156	4.03	3.37	2.18	7.80
Conductivity	64	2500	2000	320	8140
Alk, field	95	32.0	0	0	470
Acidity	151	909	315	-358	9220
Sulfate	156	1750	1220	67.5	1100
Aluminum	156	68.4	15.6	0	930
Antimony	120	0.006	0	0	0.200
Arsenic	142	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 CaCO₃, 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.



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 CO₂ (Stumm and Morgan 1996, Hem 1985, Butler 1991). Anoxic mine water environments commonly contain high CO₂ 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 CaCO₃) is capable of being dissolved. However, CO₂ levels can be much higher within soil and mine spoil than in the atmosphere, from 0.01 to 0.10. At these CO₂ 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.

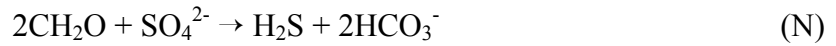
Since Turner and McCoy described their findings in 1990, dozens of additional limestone treatment systems have been constructed (e.g., Brodie et al. 1991, Skousen and Faulkner 1992). These passive mine water pretreatment systems have become known as anoxic limestone drains (ALDs). In an ALD, mine water 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 CO₂ within the treatment system, allowing the development of high CO₂ 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,



where CH_2O is used to represent organic matter. Bacterial sulfate reduction is limited to certain environmental conditions (Postgate 1984). Bacteria require 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.

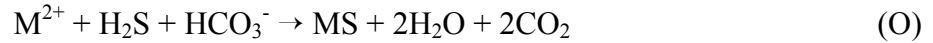
Passive treatment systems function by retaining contaminated mine water long enough to decrease contaminant concentrations to acceptable levels. The chemical and biological processes that remove contaminants vary among metals and are affected by the mine water pH and oxidation-reduction potential (Eh). 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, $\text{Fe}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$, 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.



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



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.

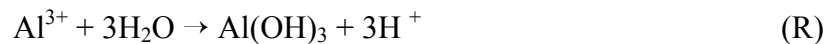
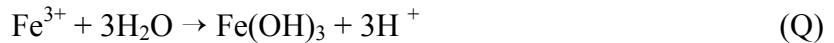
The precipitation of metal sulfides in an organic substrate improves water quality by decreasing mineral acidity without causing a parallel increase in proton acidity. Proton-releasing aspects of the H_2S dissociation process ($H_2S \rightarrow 2H^+ + S^{2-}$) are neutralized by an equal release of bicarbonate 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 iron and 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:



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., $< 5^\circ\text{C}$) 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.

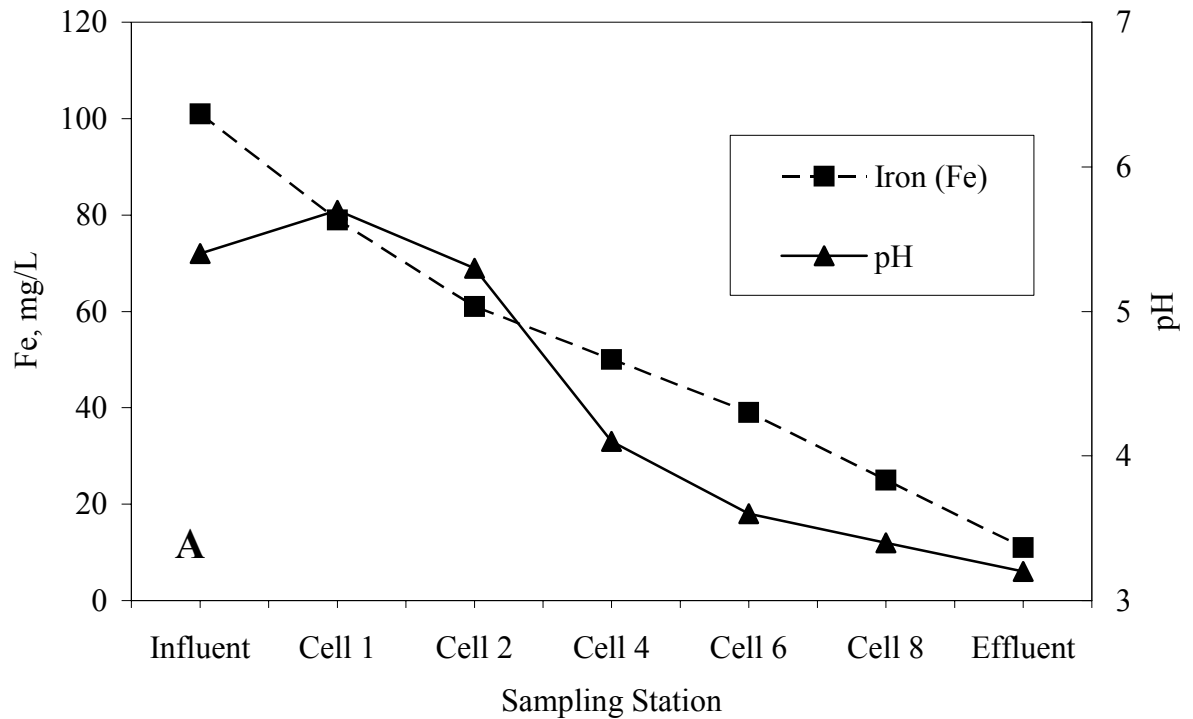


Figure 2a. Concentration of Iron and Field pH at the Emlenton Constructed Wetlands, which Receives Net Acidic Water

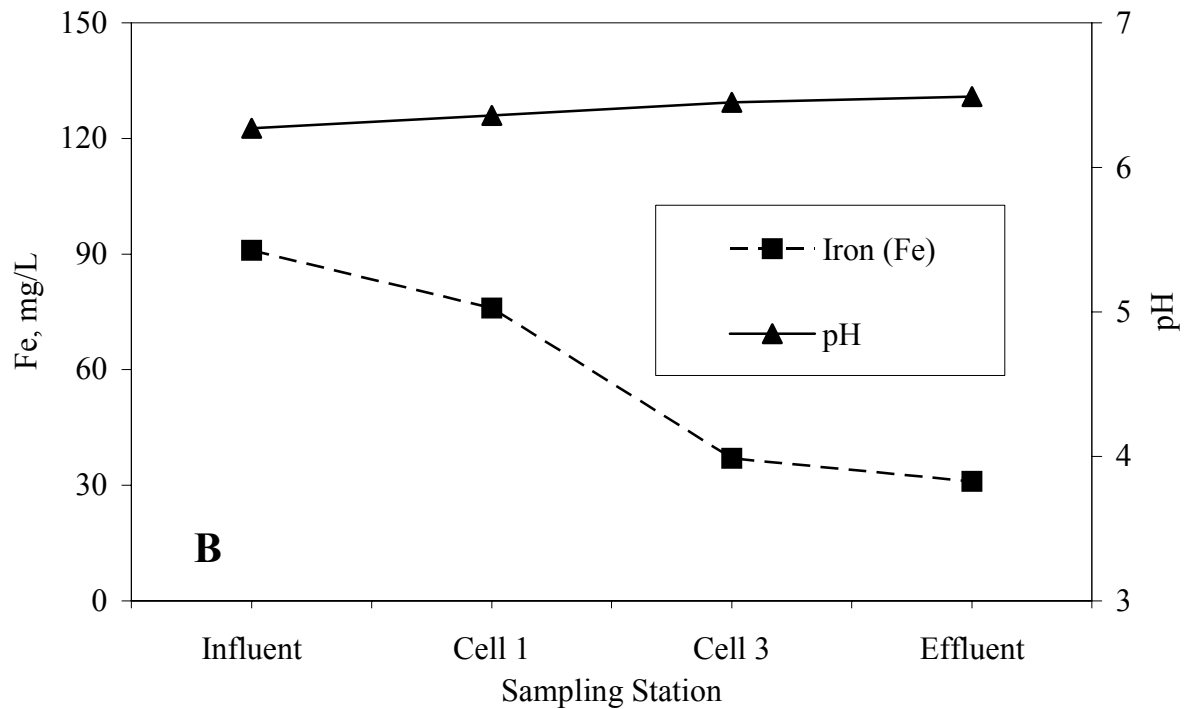


Figure 2b. Concentration of Iron and Field pH at Cedar Grove Constructed Wetlands which Receives Net Alkaline Water

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.

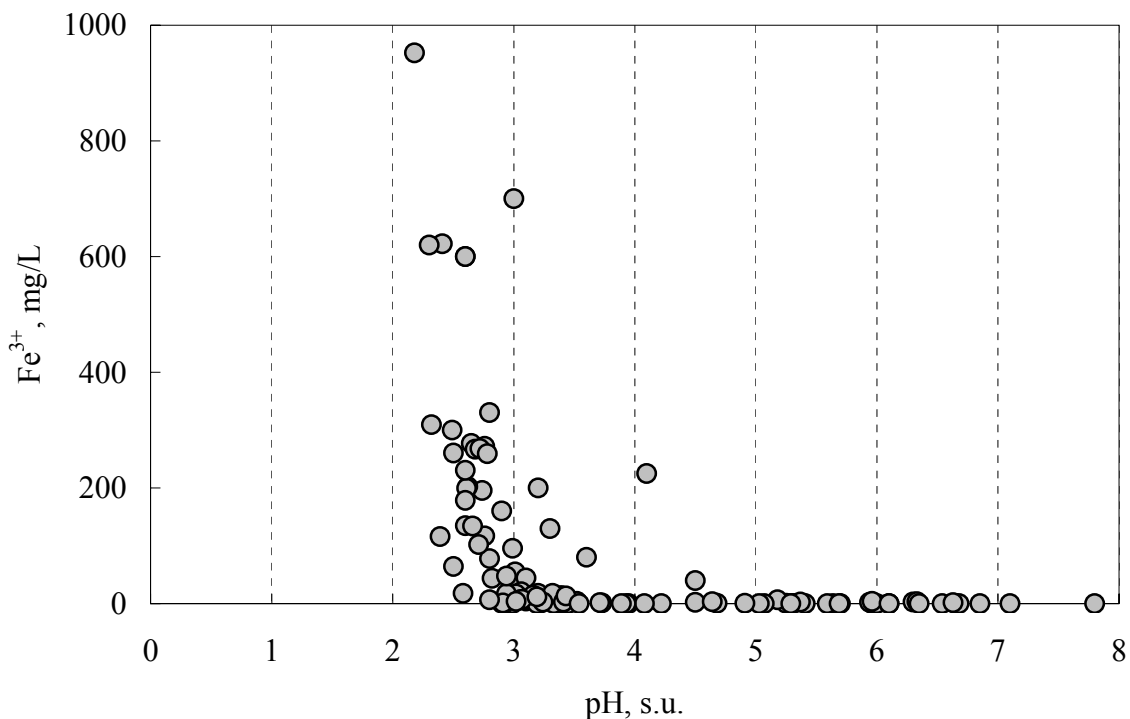


Figure 3. Dissolved Ferric Iron Concentration Versus pH in Coal Mine Discharge

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.

$$d [\text{Fe(II)}] / dt = -k [\text{Fe(II)}] [\text{O}_2] [\text{H}^+]^{-2} \quad (3)$$

As can be seen from the inverse second order dependence on $[\text{H}^+]$, 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 $18 \text{ mg L}^{-1} \text{ hr}^{-1}$, while the rate for the raw acidic samples was only $1.4 \text{ mg L}^{-1} \text{ hr}^{-1}$. 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.

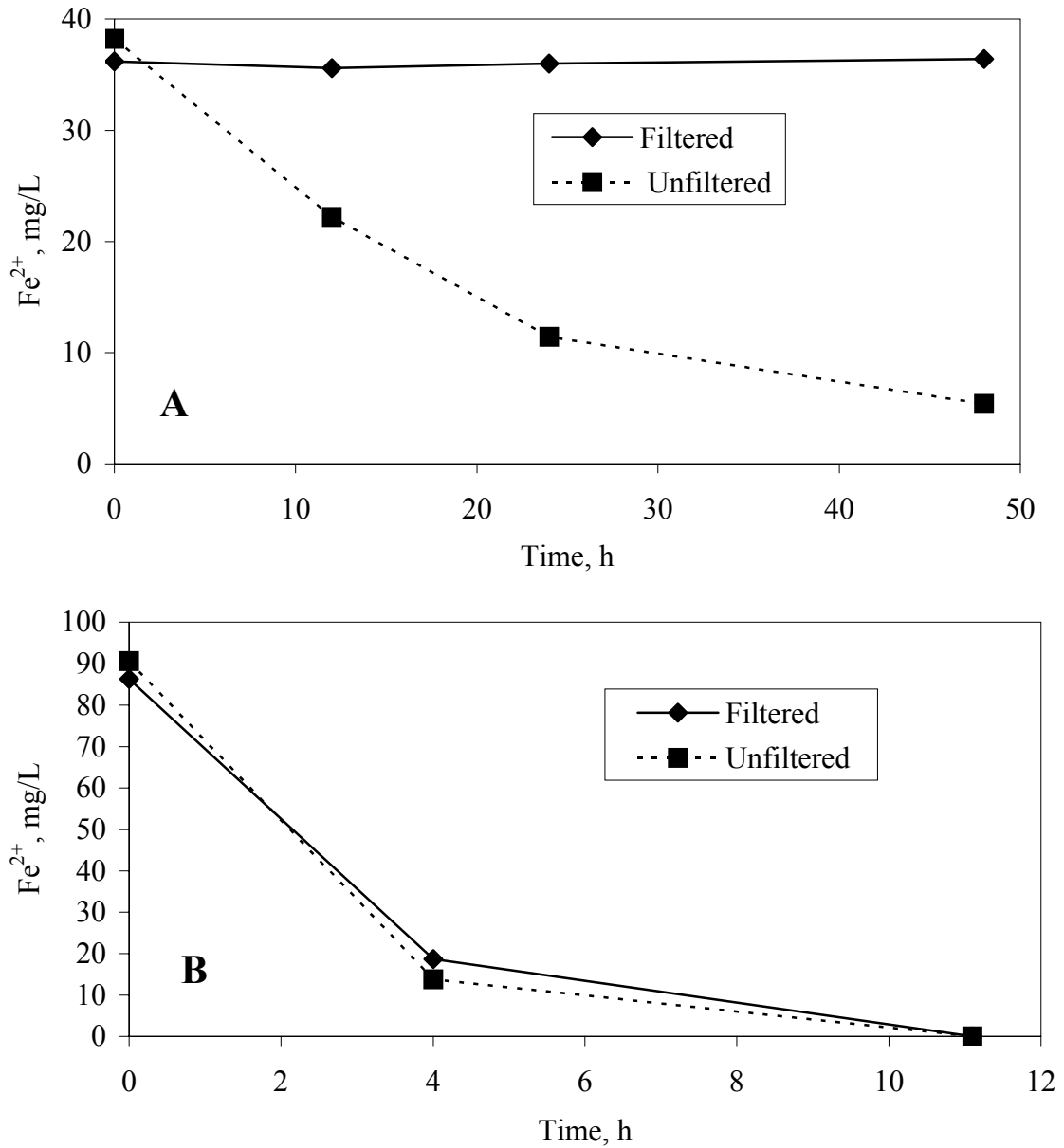


Figure 4. Removal of Ferrous Iron from Acidic and Alkaline Mine Waters in a Laboratory Experiment

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, $[Bact]$.

$$d [Fe(II)] / dt = - k_{bio} [Bact] [H^+] [Fe(II)] [O_2] \quad (4)$$

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.

$$d [Fe(II)] / dt = - k_{hetero} [Fe(III)][Fe(II)] [O_2] [H^+]^{-1} \quad (5)$$

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 $[OH^-]$ 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.

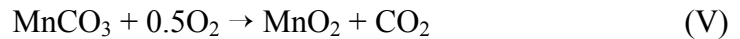
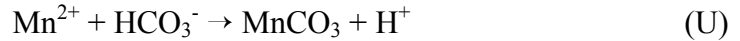
Rate constants increase with increasing temperature. To quantitatively model the iron loss in a system where the temperature is not constant, the temperature dependence is usually expressed as the exponential given in equation 6 (Kirby et al. 1999, Watzlaf et al. 2001).

$$k = A e^{\frac{-E_{act}}{RT}} \quad (6)$$

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).



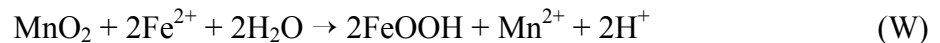
Regardless of the mechanism by which Mn^{2+} is oxidized to Mn^{4+} , the removal of one mole of Mn^{2+} from solution results in the release of two moles of H^+ , or an equivalent decrease in alkalinity (HCO_3^-).

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.



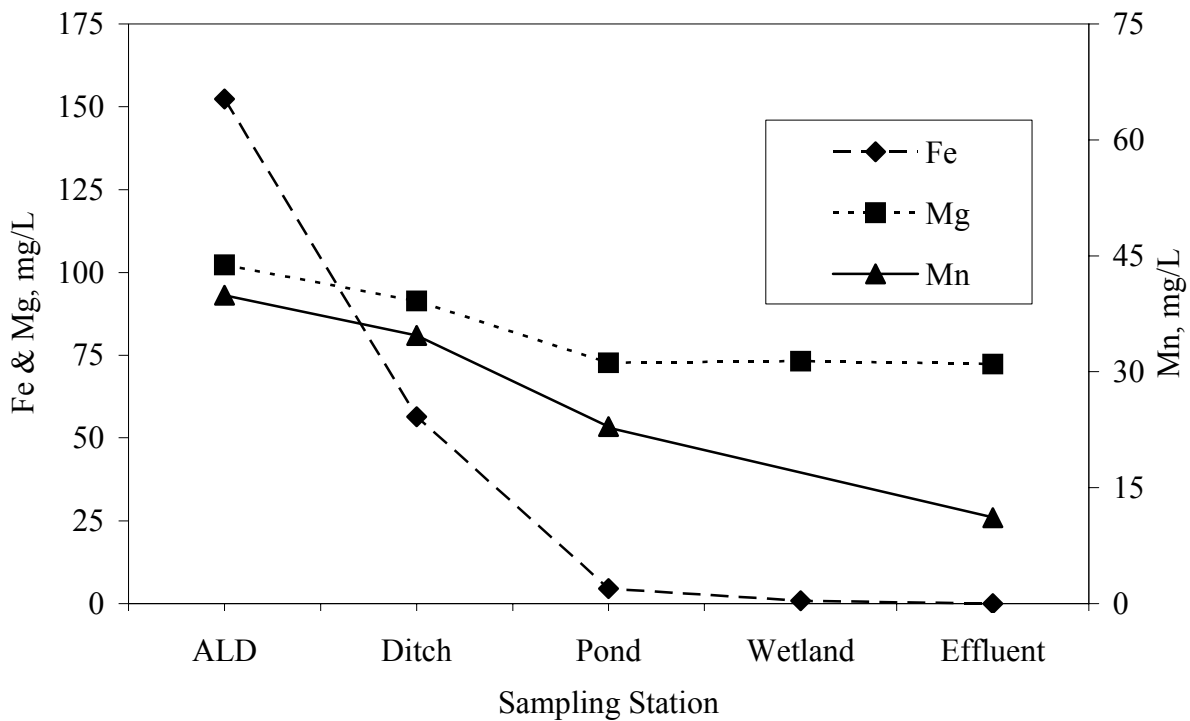


Figure 5. Mean Concentration of Iron, Manganese and Magnesium at the Morrison Wetland as the Mine Water Flows Linearly through the System

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.

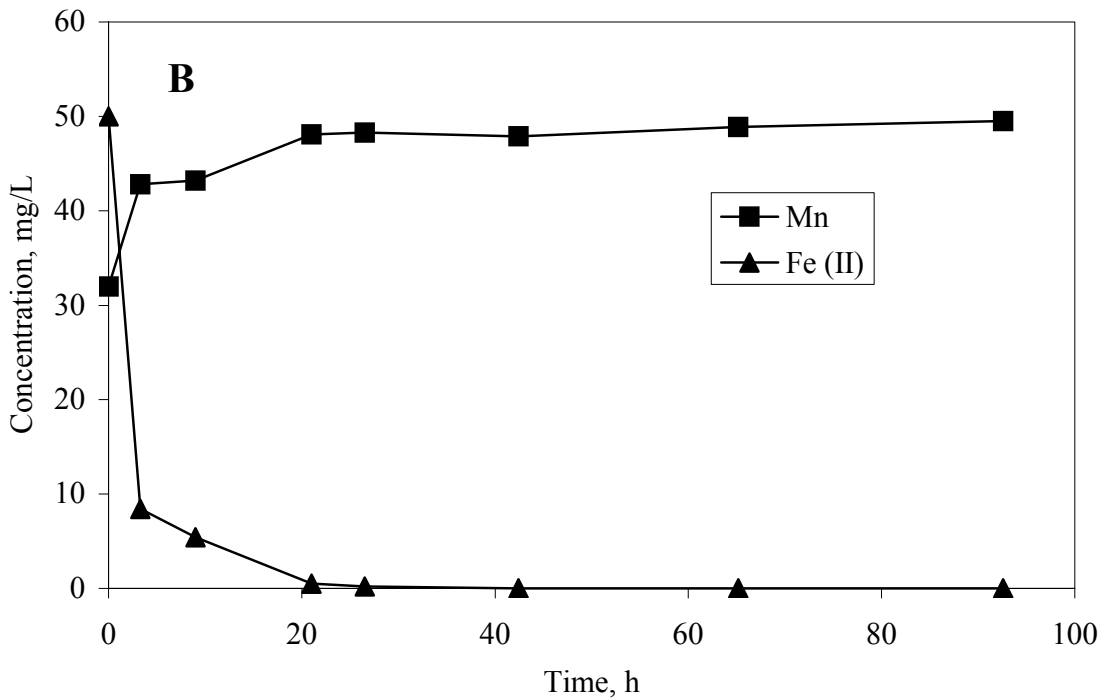
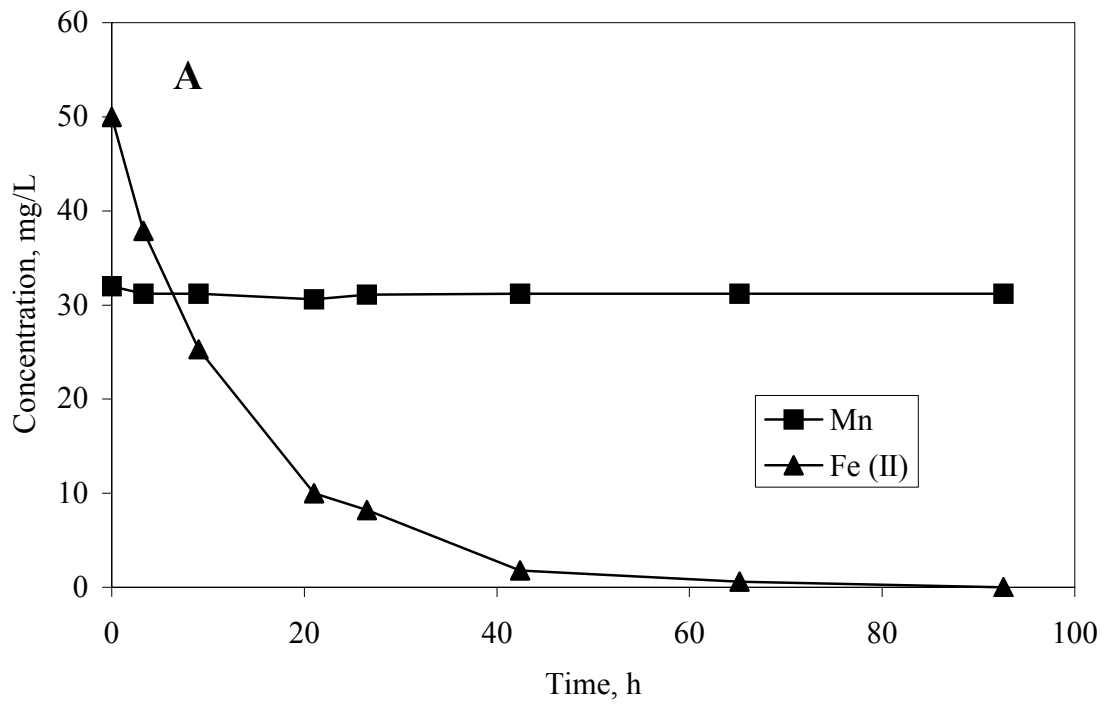


Figure 6. Changes in the Concentrations of Ferrous Iron and Manganese in (A) the Absence of the MnOOH and (B) the Presence of MnOOH

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 $\text{Al}(\text{OH})_3$ (Hem 1985, Nordstrom and Ball 1986). At pH levels between 5 and 8, $\text{Al}(\text{OH})_3$ is insoluble, and concentrations of dissolved aluminum are usually less than 1 mg/L. At pH values less than 4, $\text{Al}(\text{OH})_3$ 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 shown 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.

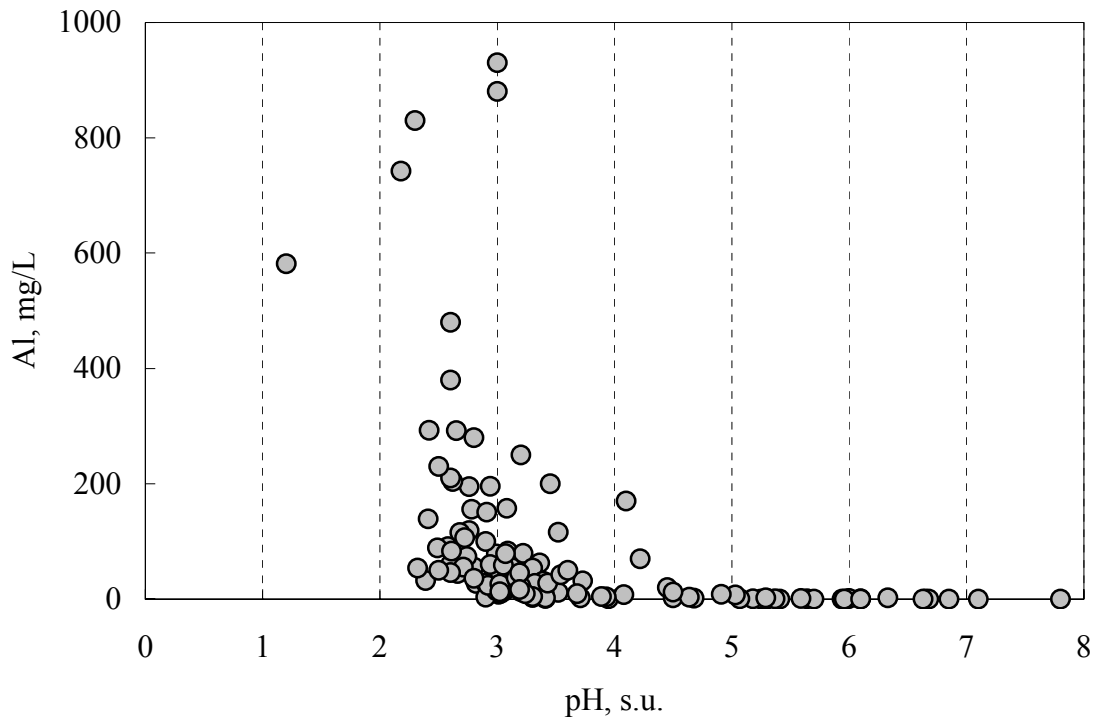


Figure 7. Dissolved Aluminum Concentration Versus pH in Coal Mine Discharges

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 aluminosilicate 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 $\text{Al}(\text{OH})_3$. In addition to $\text{Al}(\text{OH})_3$, 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 [$\text{Al}_2(\text{SO}_4)(\text{OH})_4 \cdot 7\text{H}_2\text{O}$] 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 cm³ 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 cm³ 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 cm³ 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:

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

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:

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

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.

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

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.

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

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 Schnepf - 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 (1 to 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.

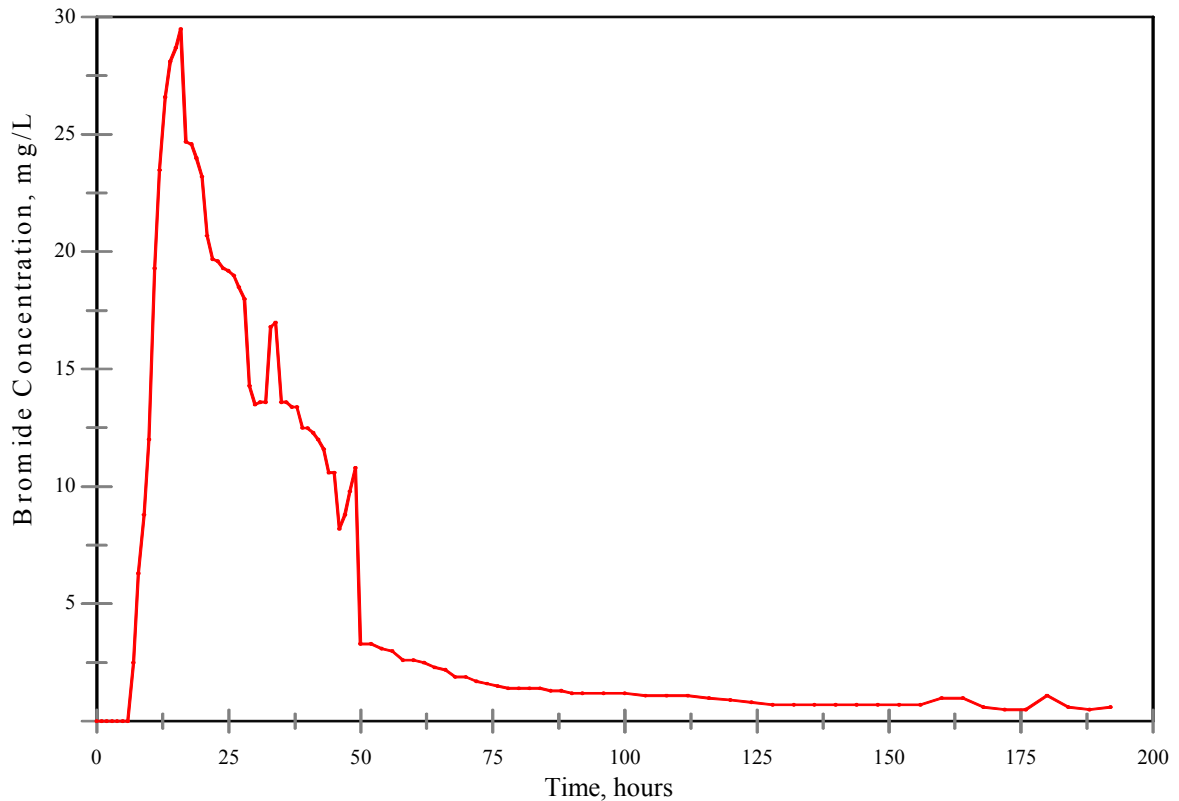


Figure 8. Bromide Concentration Versus Time in the Effluent of the Howe Bridge ALD 1 Resulting from a Pulse Input of a Bromide Tracer

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 time ¹ , hrs	40	87
Calculated detention time ² , hrs	25	47

¹Effective detention time (t_e) calculated by $t_e = \Sigma[(C_i t)\Delta t]/E(C_i \Delta t)$, where C_i = bromide concentration at time t , t = time after tracer addition, and Δt = time between samples. ²Calculated 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.

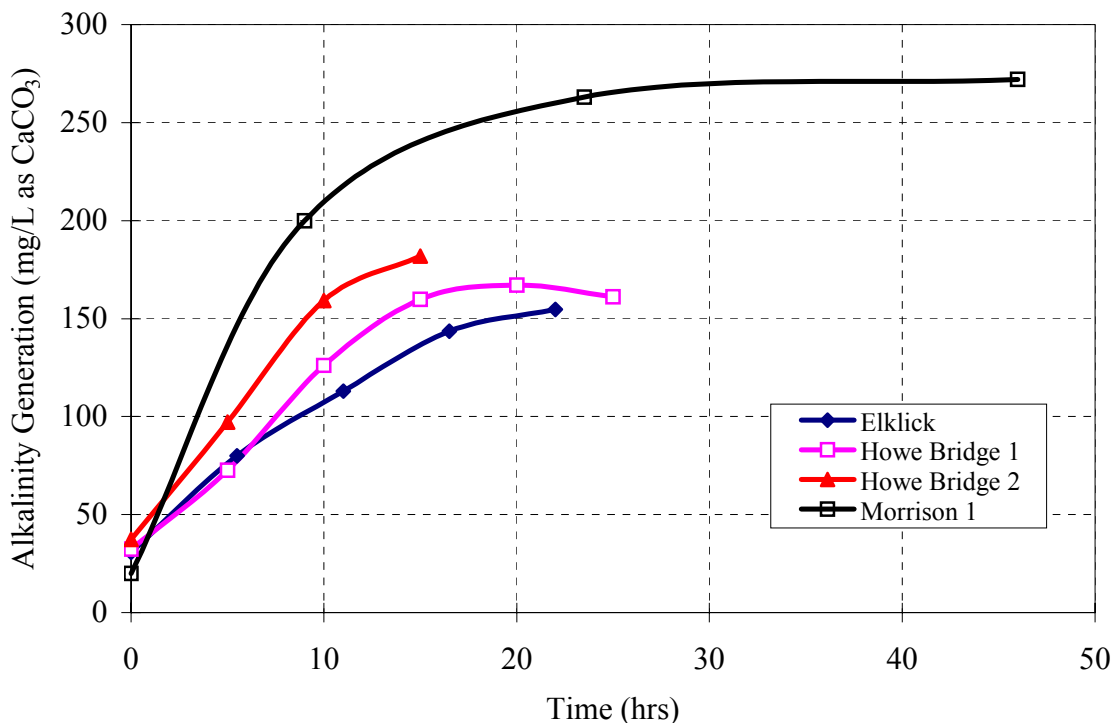


Figure 9. Alkalinity Concentration as Mine Water Flows through Selected ALD

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 , $((\text{calcium out} - \text{calcium in}) / (\text{alkalinity out} - \text{alkalinity in}))$ 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.

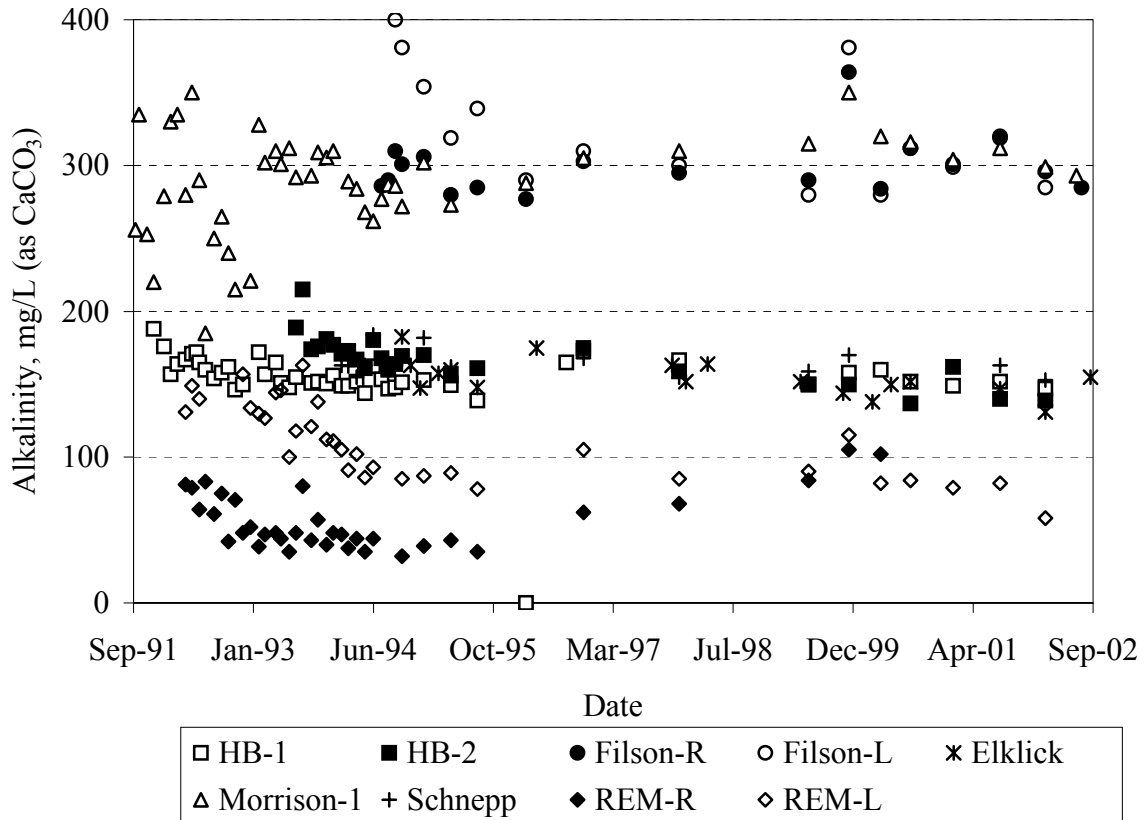


Figure 10. Effluent Alkalinity Concentrations of Selected ALDs Over Time

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 Schnepf), based influent water quality on historical data.

Table 10. Initial and Current Conditions of ALDs

ALD Site	Year Built	Initial Conditions		Avg. Flow L/min	Current Conditions		Year when $t_d = 15$ hours
		Limestone tonnes	t_d^1 hrs		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 losses, 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 Schnepf 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 Schnepf 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 decreased 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 $12 \text{ g d}^{-1} \text{ m}^{-2}$. 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 $7 \text{ g d}^{-1} \text{ m}^{-2}$. 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.



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 than 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 CaCO₃); (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 CaCO₃); (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 CaCO ₃	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⁻¹m⁻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. ²Jennings contained a compost and limestone mixture, the 25-hr td is for the mixed layer. ³Total 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 $19.6 \text{ g d}^{-1} \text{ m}^{-2}$ 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 $39 \text{ g d}^{-1} \text{ m}^{-2}$.

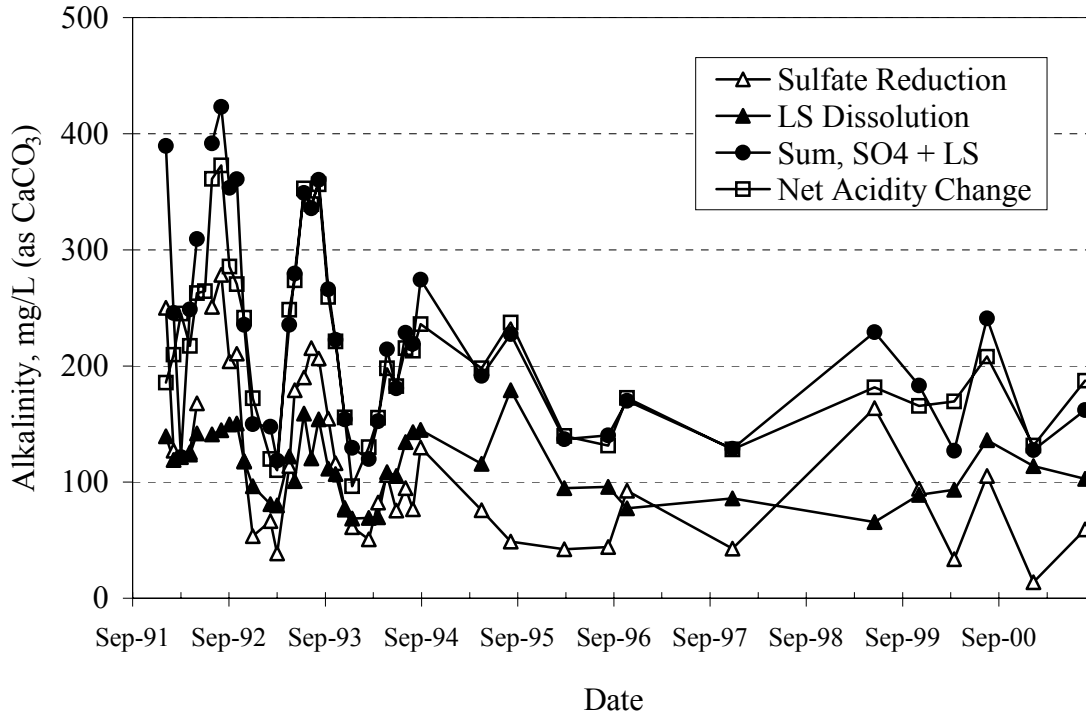


Figure 11. Alkalinity Generation in the Howe Bridge RAPS

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 $57.4 \text{ gd}^{-1}\text{m}^{-2}$, and the second at a rate of $20.6 \text{ gd}^{-1}\text{m}^{-2}$ over five years of operation. Similarly, at site E, the first RAPS produced alkalinity at a rate of $42.7 \text{ gd}^{-1}\text{m}^{-2}$, and the second at a rate of $15.6 \text{ gd}^{-1}\text{m}^{-2}$, 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 CaCO ₃	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 ° 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 through 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 m³ of iron sludge was retained in the RAPS. Making similar assumptions for the aluminum sludge results in 2.92 m³ of aluminum sludge, for a total sludge volume of 8.50 m³. Assuming a 25 percent void in the compost and a 50 percent void in the limestone, the RAPS contains about 595 m³ 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-section of 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 ($\text{Ca}(\text{OH})_2$), 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 (H₂O₂ 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 system. 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, Schnepf, 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 ₂ O 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 Ponds sand Wetlands	Anoxic Limestone Drains	Reducing and Alkalinity Producing Systems

* pH in standard units, concentrations in mg/L, acidity in mg/L as CaCO₃

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.

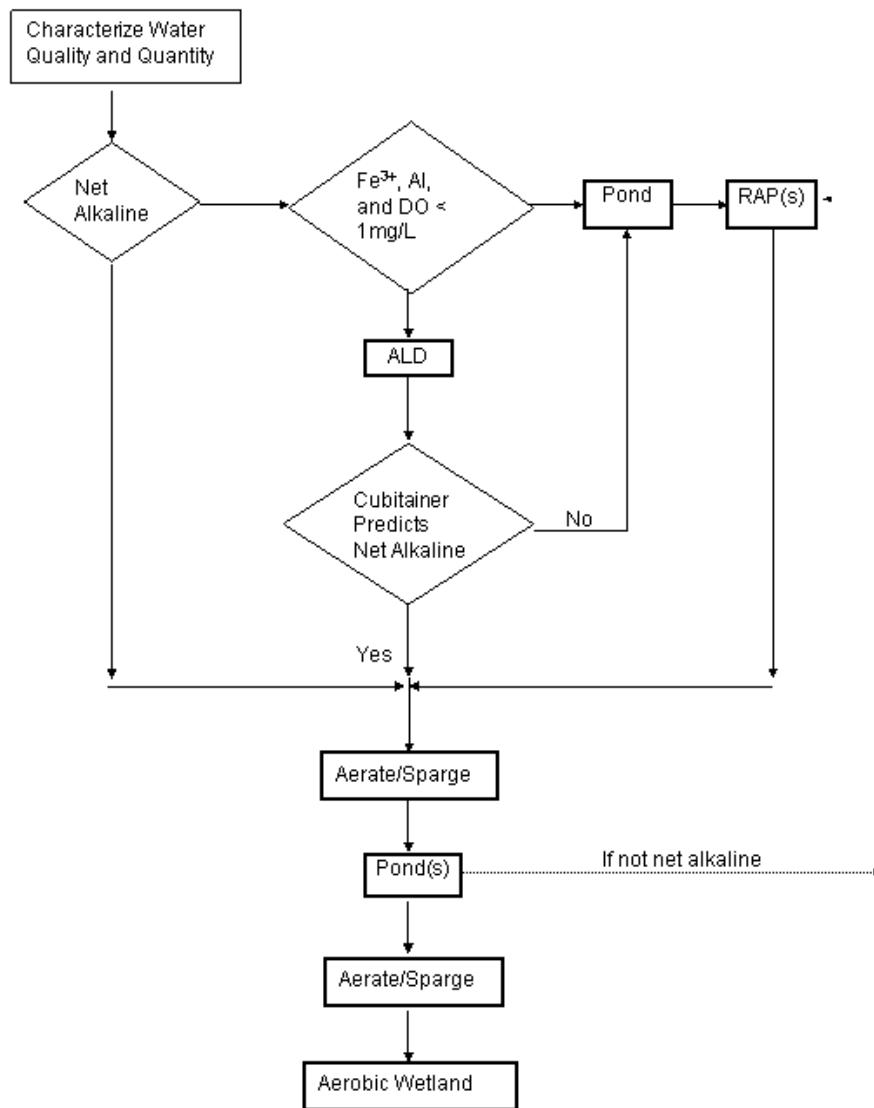


Figure 12. Selection of Passive Treatment Unit Operations

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:

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

Aerobic Ponds and Wetlands

Sizing criteria for abandoned mined land (AML) uses $20 \text{ g d}^{-1} \text{ m}^{-2}$ for iron, and $1.0 \text{ g d}^{-1} \text{ m}^{-2}$ 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 ($20 \text{ g d}^{-1} \text{ m}^{-2}$) 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 ($10 \text{ g d}^{-1} \text{ m}^{-2}$) 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 ($0.5 \text{ g d}^{-1} \text{ m}^{-2}$) is based on the performance of five treatment systems, three of which consistently lower manganese concentrations to compliance levels. A higher removal value ($1 \text{ g d}^{-1} \text{ m}^{-2}$), is suggested for AML sites. Because the toxic effects of manganese at moderate concentrations ($< 50 \text{ mg/L}$) 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 $\text{Al}(\text{OH})_3$) 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 of greater 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 CaCO₃ 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).

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

$$M_c = (\text{flow} \times \text{alkalinity concentration} \times \text{design lifetime}) / \text{CaCO}_3 \text{ content} \quad (13)$$

There are still some concerns about the ability of ALDs to maintain unchanneled flow for a prolonged period of time, how much of the CaCO₃ 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 Fe²⁺ 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 Fe²⁺ 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 (Fe³⁺) or aluminum, higher concentrations of acidity can be treated with an ALD than when the water is contaminated with only Fe²⁺ and manganese. This enhanced performance results from a decrease in mineral acidity due to the hydrolysis and precipitation of Fe³⁺ 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 $40 \text{ g d}^{-1} \text{ m}^{-2}$ of acidity for the initial system, and $15 \text{ g d}^{-1} \text{ m}^{-2}$ 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 - $50 \text{ g d}^{-1} \text{ m}^{-2}$ for the 12 systems that they studied, and suggested using $25 \text{ g d}^{-1} \text{ m}^{-2}$ as a design criteria for RAPS. Thomas and Romanek (2002) found alkalinity generation rates averaged $88 \text{ g d}^{-1} \text{ m}^{-2}$ 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 - $30 \text{ g d}^{-1} \text{ m}^{-2}$ for the first RAPS in a series, and $15 \text{ g d}^{-1} \text{ m}^{-2}$ 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 cm³ 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 CaCO₃ content (> 80 percent) has been

shown to dissolve faster than limestone with a higher MgCO_3 or $\text{CaMg}(\text{CO}_3)_2$ 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 CaCO₃. 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 CaCO₃. 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 designing 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

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