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Passive Treatment of Coal Mine Drainage

By Robert S. Hedin, Robert W. Narin,
and Robert L. P. Kleinmann

UNITED STATES DEPARTMENT OF THE INTERIOR

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Passive methods of treating mine water utilize chemical and biological processes that decrease metal concentrations and neutralize acidity. Compared to conventional chemical treatment, passive methods generally require more land area, but utilize less costly reagents and require less operational attention and maintenance. Currently, three types of passive technologies exist: aerobic wetlands, wetlands that contain an organic substrate, and anoxic limestone drains. Aerobic wetlands promote mixed oxidation and hydrolysis reactions, and are most effective when the raw mine water is net alkaline. Organic substrate wetlands promote anaerobic bacterial activity that results in the precipitation of metal sulfides and the generation of bicarbonate alkalinity. Anoxic limestone drains generate bicarbonate alkalinity and can be useful for the pretreatment of mine water before it flows into a wetland.

Rates of metal and acidity removal for passive systems have been developed empirically. Aerobic wetlands remove Fe and Mn from alkaline water at rates of 10-20 $g \cdot m^{-2} \cdot d^{-1}$ and 0.5-1.0 $g \cdot m^{-2} \cdot d^{-1}$, respectively. Wetlands with a composted organic substrate remove acidity from mine water at rates of 3-9 $g \cdot m^{-2} \cdot d^{-1}$. A model for the design and sizing of passive treatment systems is presented in this report.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	$L \cdot min^{-1}$	liter per minute
°C	degree Celsius	m	meter
ft	foot	m^2	square meter
g	gram	μm	micrometer
$g \cdot cm^{-3}$	*gram per cubic centimeter*	*meq*	*milliequivalent*
$g \cdot d^{-1}$	gram per day	mg	milligram
$g \cdot m^{-2}$	gram per square meter	$mg \cdot L^{-1}$	milligram per liter
$g \cdot m^{-2} \cdot d^{-1}$	gram per square meter per day	$mg \cdot L^{-1} \cdot h^{-1}$	milligram per liter per hour
$g \cdot m^{-2} \cdot yr^{-1}$	gram per square meter per year	mL	milliliter
gpm	gallon per minute	*min*	minute
ha	hectare	nmol	nanomole
h	hour	$nmol \cdot cm^{-3} \cdot d^{-1}$	nanomole per cubic centimeter per day
kg	kilogram (concentration)	yd^2	square yard
$kg \cdot d^{-1}$	kilogram per day	yr	year
$kg \cdot m^{-3}$	kilogram per cubic meter		
L	liter		

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PASSIVE TREATMENT OF COAL MINE DRAINAGE

By Robert S. Hedin,[1] Robert W. Nairn,[2] and Robert L. P. Kleinmann[3]

ABSTRACT

Passive methods of treating mine water use chemical and biological processes that decrease metal concentrations and neutralize acidity. Compared with conventional chemical treatment, passive methods generally require more land area, but use less costly reagents and require less operational attention and maintenance. Currently, three types of passive technologies exist: aerobic wetlands, organic substrate wetlands, and anoxic limestone drains. Aerobic wetlands promote mixed oxidation and hydrolysis reactions, and are most effective when the raw mine water is net alkaline. Organic substrate wetlands promote anaerobic bacterial activity that results in the precipitation of metal sulfides and the generation of bicarbonate alkalinity. Anoxic limestone drains generate bicarbonate alkalinity and can be useful for the pretreatment of mine water before it flows into a wetland.

Rates of metal and acidity removal for passive systems have been developed empirically by the U.S. Bureau of Mines. Aerobic wetlands remove Fe and Mn from alkaline water at rates of 10-20 and 0.5-1.0 $g \cdot m^{-2} \cdot d^{-1}$, respectively. Wetlands with a composted organic substrate remove acidity from mine water at rates of 3-9 $g \cdot m^{-2} \cdot d^{-1}$. A model for the design and sizing of passive treatment systems is presented in this report.

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INTRODUCTION

TREATMENT OF MINE WATER

The mining of coal in the Eastern and Midwestern United States can result in drainage that is contaminated with high concentrations of dissolved iron, manganese, aluminum, and sulfate. At sites mined since May 4, 1984, drainage chemistry must meet strict effluent quality criteria (table 1). To meet these criteria, mining companies commonly treat contaminated drainage using chemical methods. In most treatment systems, metal contaminants are removed through the addition of alkaline chemicals (e.g., sodium hydroxide, calcium hydroxide, calcium oxide, sodium carbonate or ammonia). 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 metal-laden sludges that accumulate in settling ponds. It is not unusual for the water treatment costs to exceed $10,000 per year at sites that are otherwise successfully reclaimed. Total water treatment costs for the coal mining industry are estimated to exceed $1,000,000 per day (*1*).[4] The high costs of water treatment place a serious financial burden on active mining companies and have contributed to the bankruptcies of many others.

Table 1.—Federal effluent limitations for coal mine drainage

Pollutant or pollutant property	Maximum for any 1 day, $mg \cdot L^{-1}$	Average of daily values for 30 consecutive days $mg \cdot L^{-1}$
Fe total	6.0	3.0
Mn total	4.0	2.0

pH between 6.0 and 9.0.

The high costs of chemical systems also limit the water treatment efforts at abandoned sites. Thousands of miles of streams and rivers in Appalachia are currently polluted by the input of mine drainage from sites that were mined and abandoned before enactment of strict effluent regulations (*2-3*). State and Federal reclamation agencies, local conservation organizations, and watershed associations all consider the treatment of contaminated coal mine discharges to be a high priority. Unfortunately, insufficient funds are available for chemical water treatment, except in a few watersheds of special value.

Natural processes commonly ameliorate mine drainage pollution. As contaminated coal mine drainage flows into and through receiving systems (streams, rivers, and lakes), its toxic characteristics decrease naturally as a result of chemical and biological reactions and by dilution with uncontaminated water. The low pH that is common to many mine drainages is raised when the water mixes with less acidic or alkaline water or through direct contact with carbonate rocks. Metal contaminants of coal mine drainage then precipitate as oxides and hydroxides under the aerobic conditions found in most surface waters. Dissolved Fe precipitates as an oxyhydroxide, staining the bottoms of many streams orange and often accumulating to sufficient depths to suffocate benthic organisms. Less commonly, dissolved Mn precipitates as an oxide that stains rocks and detrital material black. Dissolved Al precipitates as a white hydroxide.

During the last decade, the possibility that mine water might be treated passively has developed from an experimental concept to full-scale field implementation at hundreds of sites. Passive technologies take advantage of natural chemical and biological processes that ameliorate contaminated water conditions. Ideally, passive treatment systems require no input of chemicals and little or no operation and maintenance requirements. The costs of passive treatment systems are generally measured in their land use requirements. Passive treatment systems use contaminant removal processes that are slower than that of conventional treatment and thus require longer retention times and larger areas to achieve similar results.

The goal of passive mine drainage treatment systems is to enhance the natural amelioration 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 minesite 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 that the nature of the rate-limiting aspects of each removal process be understood.

This U.S. Bureau of Mines (USBM) report describes the chemical and biological processes that underlie the passive technologies currently used in the eastern United States for the treatment of contaminated coal mine drainage. After reviewing the background of passive treatment and the methods used in these studies (Chapter 1), the chemical behavior of mine drainage contaminants is reviewed (Chapter 2). This discussion highlights the difference between alkaline and acidic mine water, and details the processes in passive treatment systems that generate alkalinity. In Chapter 3, contaminant removal is

[4]Italic numbers in parentheses refer to items in the list of references at the end of this report.

evaluated for 13 passive treatment systems through the calculation of contaminant removal rates. These rates, which incorporate the size of the treatment system, the flow rate of the water, and mine drainage chemistry, are the only measures of treatment system performance that can be reliably compared between systems. In Chapter 4, the chemical background provided in Chapter 2 and the observed contaminant removal rates presented in Chapter 3 are combined in a model that gives design and sizing recommendations for future passive treatment systems. Chapter 5 summarizes the results of this study and identifies future research needs.

BACKGROUND OF PASSIVE TREATMENT

The current interest in passive treatment technologies can be traced to two independent research projects that indicated that natural *Sphagnum* wetlands caused an amelioration of mine drainage pollution without incurring any obvious ecological damage (*4-5*). These observations prompted the idea that wetlands might be constructed for the intentional treatment of coal mine drainage. Research efforts were initiated by West Virginia University, Wright State University, Pennsylvania State University, and the USBM to evaluate the feasibility of the idea. As a result of promising preliminary reports (*6-8*), experimental wetlands were built by mining companies and reclamation groups. Initially, most of these wetlands were constructed to mimic *Sphagnum* moss 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 (*9-10*). 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 consist of a series of small wetlands (<1 ha) that are vegetated with cattails (*Typha latifolia*) (*11-12*). In northern Appalachia, many wetlands contain a compost and limestone substrate in which the cattails root. In southern Appalachia, most wetlands have been constructed without an exogenous organic substrate; emergent plants have been rooted in whatever soil or spoil substrate was available on the site when the treatment system was constructed (*13*).

Recently, treatment technologies have been developed that do not rely at all on the wetland model that the early systems were designed to mimic. Ponds, ditches, and rock-filled basins have been constructed that are not planted with emergent plants, and in some cases, contain no soil or organic substrate (*14*). Pretreatment systems have been developed where acidic water contacts limestone in an anoxic environment before flowing into a settling pond or wetland system (*15*). In these cases, the water is treated with limestone followed by passive aeration; however, the low cost and chemical behavior of limestone make possible the construction of wetland systems that should, theoretically, require no maintenance and last for decades.

A wide diversity of opinions exist on the merits of passive treatment systems for mine drainage. Wieder's analysis of a survey of constructed wetlands conducted by the Office of Surface Mining (OSM) indicated no strong relationships between concentration efficiency and wetland design features, leading him to question the feasibility of the constructed wetland concept (*12*). In a separate study by Wieder and his colleagues, measurements of the Fe content of *Sphagnum* peat exposed to synthetic acid mine drainage were used to calculate that an average wetland system should cease to remove metals after 11 weeks of operation (*16*). These negative reports contrast with many other studies of successful wetlands. Examples include an Ohio wetland that is treating Fe-contaminated mine drainage effectively in its 8th year of operation (*17*) and six Tennessee Valley Authority (TVA) wetlands that have produced compliance water for at least 4 years (*18*). A vast majority of the passive treatment systems constructed in the United States during the last decade achieve performance that is better than Wieder and his colleagues would predict, though not necessarily enough to consistently meet effluent limits. Hundreds of constructed wetlands discharge water that contains lower concentrations of metal contaminants than was contained 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. In general, the systems that are not 100% effective were improperly designed, were undersized, or both. This report has been prepared so that designers of future systems can avoid these errors.

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CHAPTER 1. 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 treatment cells within the system. Raw and acidified (2 mL of concentrated HCl) water samples were collected in 250 mL plastic bottles at each sampling point. Measurements of pH and temperature were made in the field with a calibrated Orion SA 270, SA 250 or SA 290 portable pH/ISE meter.[5] Alkalinity was measured in the field using a pH meter and an Orion Total Alkalinity Test Kit. At sites where particulates were visible in water samples, an extra sample was collected that was filtered through a 0.22-μm membrane filter before acidification. All samples were immediately placed on ice in an insulated cooler and returned to the laboratory within 36 h of collection. Samples were refrigerated at 4° C until analysis.

Substrate pore water samples were collected using a dialysis method similar to that described by Wheeler and Giller (*19*). Lengths of 6,000-8,000 molecular weight dialysis tubing were filled with 250 mL of deionized, deoxygenated water and buried 30-45 cm deep in the organic substrate of the wetland. Three weeks later, the dialysis tubes were retrieved and the contents immediately filtered through a 0.45-μm membrane filter. Laboratory experiments established that the chemistry of water within the sampling tubes equilibrated with surrounding pore water within 24 h. The 3-week equilibration period was allowed so that chemical anomalies caused by the burial process would dissipate. Portions of the filtered water samples were preserved with NaOH (for dissolved sulfide determinations), HCl (for cation analysis), or were left unpreserved (for alkalinity, acidity, and sulfate analyses).

ANALYSIS OF WATER SAMPLES

Concentrations of Fe, Mn, Al, Ca, Mg, and Na were determined in the acidified samples using Inductively Coupled Argon Plasma Spectroscopy, ICP (Instrumentation Laboratory Plasma 100 model). The acidified samples were first filtered through a 0.45-μm membrane filter to prevent clogging of the small diameter tubing in the ICP.

Ferrous iron concentrations were determined on acidified samples by the potassium dichromate method (*20*). Sulfate concentrations were determined by reaction with barium chloride (BaCl) after first passing the raw sample through a cation exchange resin. Thorin was used as the end-point indicator. Dissolved sulfide species were determined using a sulfide-specific electrode.

Acidity was determined by boiling a 50-mL raw sample with 1 mL of 30% H_2O_2 (hydrogen peroxide), and then titrating the solution with 0.1 *N* NaOH (sodium hydroxide) to pH 8.3 (*21*). Acidity and alkalinity are reported as $mg \cdot L^{-1}$ $CaCO_3$ equivalents.

ANALYTICAL QUALITY CONTROL

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 the duplicate was always at least 95%. Percent recovery for the standards were within 3% of the original standard. Spike recoveries were within 5% of the expected values.

FLOW RATE MEASUREMENTS

Mine water flow rates were determined by several methods. Whenever possible, flow was determined with a bucket and stopwatch. In all cases, three to five measurements of the time needed to collect a known volume of water were made at each sampling location, and the average flow rate of these measurements was reported. At two sites where flows were occasionally too high to measure with a bucket (the Latrobe and Piney Wetlands), 0.50 or 0.75 ft H-type flumes were installed and flows were determined from the depth of water in the flume. At the Keystone site, flows were determined by measuring the depth of water in a drainage pipe and then using the Manning formula for measurement of gravity flow in open channels (*22*).

ANALYSIS OF SURFACE DEPOSITS

The chemical composition of surface deposits collected from several constructed wetlands were determined by the following procedure. The samples were rinsed with deionized water, dried at 100° C, and weighed. The acid-soluble component was extracted by boiling 5 g of dry sample in 20 mL of concentrated HCl for 2 min. The acid extractants were filtered and analyzed for metal content by ICP Spectroscopy and for sulfate content by liquid chromatography. The acid-insoluble material was dried at 100° C and weighed. The acid-soluble component was determined by subtracting the dry weight of the insoluble material from the original dry weight.

[5]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

CHAPTER 2. CHEMICAL AND BIOLOGICAL PROCESSES IN PASSIVE TREATMENT SYSTEMS

Coal mining can promote pyrite oxidation and result in drainage containing high concentrations of Fe, Mn, and Al, as well as SO_4, Ca, Mg, and Na. The solubilities of Fe, Mn, and Al are generally very low (<1 mg•L^{-1}) in natural waters because of chemical and biological processes that cause their precipitation in surface water environments. The same chemical and biological processes remove Fe, Mn, and Al from contaminated coal mine drainage, but the metal loadings from abandoned minesites 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 between 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.

This chapter provides the basic chemical and biological background necessary to efficiently design passive treatment systems. The authors begin with a discussion of acidity and alkalinity because many of the decisions about how to treat mine water passively depend on determinations of these parameters. Next, the chemistry of Fe, Mn, and Al in aerobic and anaerobic aquatic environments is described. Throughout the discussion, chemical and biological concepts are illustrated with data collected from passive treatment systems.

ACIDITY

Acidity is a measurement of the base neutralization capacity of a volume of water. Three types of acidity exist: proton acidity associated with pH (a measure of free H^+ ions), organic acidity associated with dissolved organic compounds, and mineral acidity associated with dissolved metals (*23*). Mine waters generally have a very low dissolved organic carbon content, so organic acidity is very low. The acidity of coal mine drainage arises from free protons (low pH) and the mineral acidity from dissolved Fe, Mn, and Al. These metals are considered acidic because they can undergo hydrolysis reactions that produce H^+.

$$Fe^{2+} + 1/4O_2 + 3/2H_2O \rightarrow FeOOH + 2H^+ \quad (A)$$

$$Fe^{3+} + 2H_2O \rightarrow FeOOH + 3H^+ \quad (B)$$

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

$$Mn^{2+} + 1/4O_2 + 3/2H_2O \rightarrow MnOOH + 2H^+ \quad (D)$$

These reactions can be used to calculate 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 acidic metals. For most coal mine drainages, the calculation is as follows:

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

where all metal concentrations are in milligram per liter and 50 is the equivalent weight of $CaCO_3$, and thus transforms milliequivalent per liter of acidity into milligram per liter $CaCO_3$ equivalent. For water samples with pH <4.5 (no alkalinity present), equation 1 calculates a mine water acidity that corresponds closely with measurements of acidity made using the standard H_2O_2 method (*21*). Using synthetic mine drainages with a wide range of compositions, it was determined that calculated acidities differed from measured values by less than 10% (table 2).

Equation 1 accurately characterizes mineral acidity for samples of actual acid mine drainage as well. At one site where numerous measurements of metal chemistry and total acidity were made, the mean acidity of samples with pH <4.5 was 693 mg•L^{-1}, while the predicted acidities for these samples averaged 655 mg•L^{-1}, a difference of only 6% (figure 1).

Equation 1 can be used to partition total acidity into its individual constituents. When the total acidities of contaminated coal mine drainages are partitioned in this manner, the importance of mineral acidity becomes apparent. A breakdown of the acidic components of three mine drainages is shown in table 3. At each site, the acidity arising from protons (pH) was a minor component of the total acidity. Mine drainage at the Friendship Hill wetland had extremely low pH (2.7), but the acidity of the

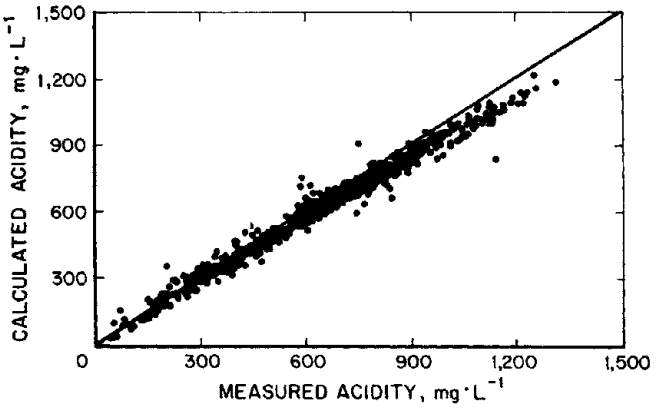

Figure 1.—Comparison of calculated and measured acidities for water samples collected at Friendship Hill wetland.

mine water resulted primarily from dissolved ferric iron and Al. The Somerset wetland received water with low pH (3.7), but the acidity of the water resulted largely from dissolved ferrous iron and Mn. At the Cedar Grove system, where the mine water was circumneutral, ferrous iron accounted for 98% of the acidity, while the hydrogen ion accounted for <1% of mine water acidity.

ALKALINITY

When mine water has pH >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 (*23*). The principal source of alkalinity in mine water is dissolved carbonate, which can exist in a bicarbonate (HCO_3^-) or carbonate form (CO_3^{2-}). Both can neutralize proton acidity.

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

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

In the pH range of most alkaline mine waters (5 to 8), bicarbonate is the principal source of alkalinity.

The presence of bicarbonate alkalinity in mine waters that contain elevated levels of metals is not unusual. Table 4 shows the chemical composition of 12 mine waters in northern Appalachia that contain alkalinity and are also contaminated with ferrous iron and Mn. None are contaminated with dissolved ferric iron or Al because the solubility of these metals is low in mine waters with pH greater than 5.5 (*23-24*).

Table 2.—Calculated and measured acidities for synthetic acidic mine water

Synthetic Mine Water Composition[1]					Acidity		
pH	Fe^{2+}	Fe^{3+}	Al	Mn	Calculated[2]	Measured[3]	Diff.[4]
3.9	98	1	0	0	181	184	-2%
3.9	0	0	106	0	598	578	+3%
3.6	0	0	0	97	192	186	+3%
3.8	13	0	47	42	370	335	+9%

[1]Measured values are the average of three tests. Metal concentrations are $mg \cdot L^{-1}$. Acidities are $mg \cdot L^{-1}$ $CaCO_3$ equivalent.
[2]From reaction 1.
[3]Data determined by the hot H_2O_2 acidity method (*21*).
[4](1.00 - meas/cal) × 100.

Table 3.—Acidic components of mine drainage influent at three passive treatment systems

Parameter	Friendship Hill			Somerset			Cedar Grove		
	Concentration, $mg \cdot L^{-1}$	Acid equivalent,[1] $mg \cdot L^{-1}$	% of total acidity	Concentration, $mg \cdot L^{-1}$	Acid equivalent,[1] $mg \cdot L^{-1}$	% of total acidity	Concentration, $mg \cdot L^{-1}$	Acid equivalent,[1] $mg \cdot L^{-1}$	% of total acidity
Fe^{2+}	7	13	1	193	345	69	95	170	98
Fe^{3+}	153	434	49	9	24	5	<1	<1	<1
Al^{3+}	58	317	36	3	17	3	<1	<1	<1
Mn^{2+}	9	16	1	59	107	21	2	4	2
pH	2.6	112	13	3.7	10	2	6.3	<1	<1

[1]$CaCO_3$ equivalents calculated from the stoichiometry of reactions A-D.

Table 4.—Chemical compositions of mine drainages that contain high concentrations of alkalinity

Location	pH	Alkalinity, mg·L^{-1}	Al, mg·L^{-1}	Fe^{2+}, mg·L^{-1}	Fe^{3+}, mg·L^{-1}	Mn, mg·L^{-1}	SO_4, mg·L^{-1}	Net alkalinity,[1] mg·L^{-1}
Ohio: Coshocton	6.1	152	<1	119	<1	2	1,325	-50
Pennsylvania:								
Cross Creek	6.3	300	<1	96	<1	2	1,260	140
Donegal	6.6	214	<1	39	<1	8	830	130
Fallston	6.2	120	<1	30	<1	3	390	66
Keystone	6.5	106	<1	37	<1	1	331	72
Latrobe	6.2	204	<1	102	<1	6	1,200	15
New Bethlehem	6.1	163	<1	51	<1	28	493	51
Possum Hollow	6.4	263	<1	32	<1	1	620	209
Sligo	5.5	93	<1	43	<1	26	1,720	-31
Somerset	6.3	275	<1	2	<1	6	750	265
St. Petersburg	6.1	255	<1	29	<1	9	250	203
Uniontown	6.3	220	<1	70	<1	3	950	95

[1]Alkalinity minus acidity.

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 greater than acidity) or net acidic (acidity greater than alkalinity). Net alkaline water contains enough alkalinity to neutralize the mineral acidity represented by dissolved ferrous iron and Mn. As these metals oxidize and hydrolyze, the proton acidity that is produced is rapidly neutralized by bicarbonate. For waters contaminated with Fe^{2+}, the net reaction for the oxidation, hydrolysis and neutralization reactions is

$$Fe^{2+} + \tfrac{1}{4}O_2 + 2HCO_3^- \rightarrow FeOOH + \tfrac{1}{2}H_2O + 2CO_2 \quad (G)$$

Reaction G indicates that net alkaline waters contain at least 1.8 mg·L^{-1} alkalinity for each 1.0 mg·L^{-1} of dissolved Fe. Waters that contain a lesser ratio are net acidic, since the oxidation and hydrolysis of the total dissolved iron content results in a net release of protons and a decrease in the pH.

METAL REMOVAL PROCESSES

Oxidation and hydrolysis reactions already discussed cause concentrations of Fe^{2+}, Fe^{3+}, Mn, and Al to commonly 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 catalysts, 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 between metals and also between abiotic and biotic processes.

METAL REMOVAL IN AEROBIC ENVIRONMENTS

Iron Oxidation and Hydrolysis

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. 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.

$$Fe^{2+} + \tfrac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}H_2O \quad (H)$$

The pH of the mine water affects the kinetics of both the abiotic and biotic processes (*25-26*). When oxygen is not limiting, the rate of abiotic Fe oxidation slows 100-fold for every unit decrease in pH. At pH values >8, the abiotic process is fast (rates are measured in seconds), while at pH values <5 the abiotic process is slow (rates are measured in days). In contrast, bacterial oxidation of ferrous iron peaks at pH values between 2 and 3, while less activity occurs at pH values >5 (*27*). The presence of bicarbonate alkalinity buffers mine water at a pH of 6 to 7, a range at which abiotic iron oxidation processes should dominate. Waters containing no alkalinity have a pH <4.5 and the removal of Fe under oxidizing conditions occurs primarily by bacterial oxidation accompanied by hydrolysis and precipitation.

The effect that pH can have on the mechanism of iron oxidation is shown by the data in figure 2. 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

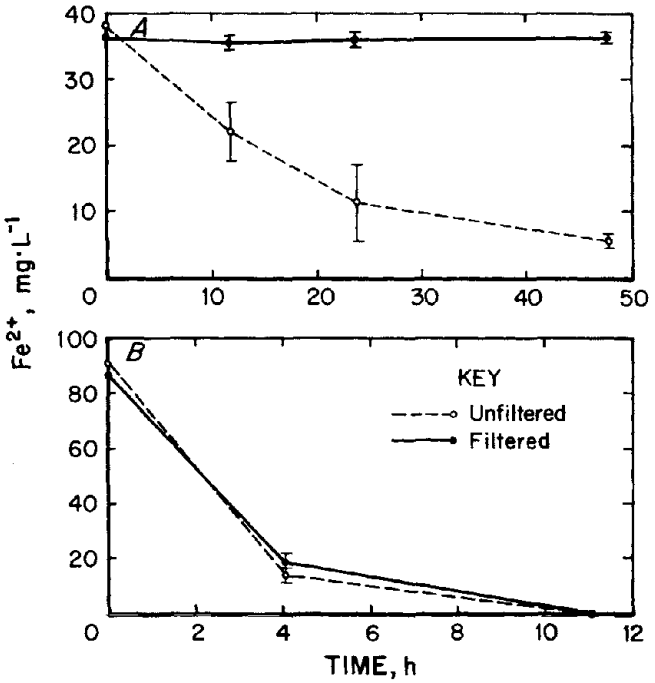

Figure 2.—Removal of Fe^{2+} from acidic and alkaline mine waters in laboratory experiment. Raw mine drainage was collected from *A*, acidic Latrobe site; *B*, alkaline Cedar Grove site. Splits of each sample were filter-sterilized (0.22-μm filter). The Latrobe samples were shaken throughout experiment; air was bubbled through Cedar Grove samples during experiment.

rate of 18 mg•L^{-1}•h^{-1}, while the rate for the raw acidic samples was only 1.4 mg•L^{-1}•h^{-1}. 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.

As ferrous iron is converted to ferric iron, it is subject to hydrolysis reactions that can precipitate it as a hydroxide (reaction B). The hydrolysis reaction occurs abiotically; catalysis of the reaction by microorganisms has not been demonstrated. The solubility of the ferric hydroxide solid is such that, under equilibrium conditions, negligible dissolved ferric iron (<1 mg•L^{-1}) exists unless the pH of the mine water is <2.5. In actuality, 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. Singer and Stumm (*25*) suggested a fourth-order relationship with pH, which indicated that ferric iron hydrolysis processes shift from a very rapid rate at pH >3 to a very slow rate at pH <2.5. Figure 3 shows the relationship between pH and concentrations of Fe^{3+} at a site where pH varied by almost 3 units. Ferric iron was not generally indicated unless the pH was <4, and the highest

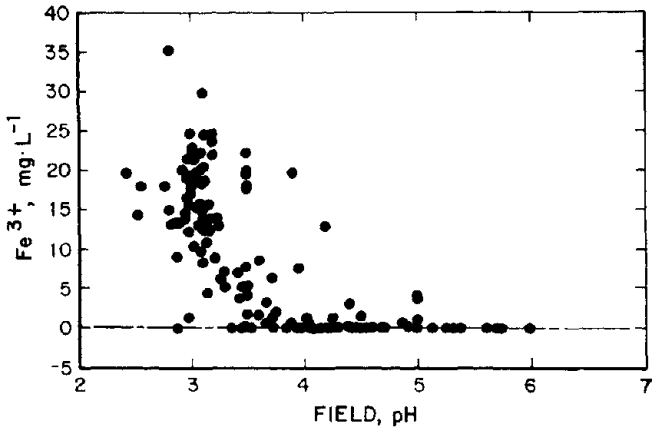

Figure 3.— Concentrations of Fe^{3+} and field pH for water samples collected from Emlenton wetland.

concentrations of ferric iron occurred when the pH was <3.

The tendency for dissolved iron to oxidize and hydrolyze in aerobic environments with pH >3 results in the precipitation of ferric hydroxide. 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 Fe concentrations and pH. An example of this phenomenon is shown in figure 4*A*. As water flowed through the constructed wetland, iron concentrations decreased from 95 to 15 mg•L^{-1}, and pH decreased from 5.5 to 3.2. Figure 4*B* shows Fe concentrations and pH within a wetland that received mine water with a net alkalinity. Despite the removal of 60 mg•L^{-1} 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.

Manganese Oxidation and Hydrolysis

Manganese undergoes oxidation and hydrolysis reactions that result in the precipitation of manganese oxyhydroxides. The specific mechanism(s) by which Mn^{2+} precipitates from acrobic mine water in the absence of chemical additions is uncertain. Mn^{2+} may be oxidized to either a +3 or a +4 valance, either one of which rapidly precipitates (reaction D). If MnOOH precipitates, over time it likely oxidizes to the more stable MnO_2. In alkaline environments, Mn^{2+} can precipitate as a carbonate, which may also be oxidized by oxygen to MnO_2 (*28*).

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

$$MnCO_3 + \tfrac{1}{2}O_2 \rightarrow MnO_2 + CO_2 \qquad (J)$$

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 <8 (*24*). Microorganisms can catalyze Mn^{2+} oxidation, but their activity is limited to aerobic waters with pH >6 (*29*).

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

The oxidation and precipitation of Mn^{2+} from solution is accelerated by the presence of MnO_2 and FeOOH (*24, 30*). Both solids reportedly act as adsorption surfaces for Mn^{2+} and catalyze the oxidation mechanism. While additions of FeOOH to Mn-containing water might accelerate Mn oxidation, the direct precipitation of FeOOH from mine water containing Fe^{2+} does not generally stimulate Mn-removal processes in passive treatment systems. Figure 5 shows concentrations of Mn and Fe for mine water as it flowed through a constructed wetland that markedly decreased concentrations of both metals. On average, Fe decreased from 150 to <1 $mg \cdot L^{-1}$, while Mn decreased from 42 to 11 $mg \cdot L^{-1}$. 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 in the concentration of Mn occurred between the first and second sampling station. The slight decrease in Mn that occurred was proportionally similar to the change in Mg, suggesting that dilution was the most likely cause of the decrease in Mn concentrations (the use of Mg to estimate dilution is discussed in detail in chapter 3). Between stations 3 and 5, there was little Fe present in the water and little visual evidence of FeOOH sludge on the wetland substrate. Most of the observed removal of Mn occurred in this Fe-free zone.

The absence of simultaneous precipitation of dissolved Fe and Mn from aerobic alkaline waters likely results from the reduction of oxidized forms of Mn by ferrous iron.

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

or

$$MnOOH + Fe^{2+} \rightarrow FeOOH + Mn^{2+} \quad (L)$$

Figure 6 shows the results of a laboratory study that demonstrate the instability of Mn oxides in the presence of ferrous iron. Water samples and Mn-oxides were

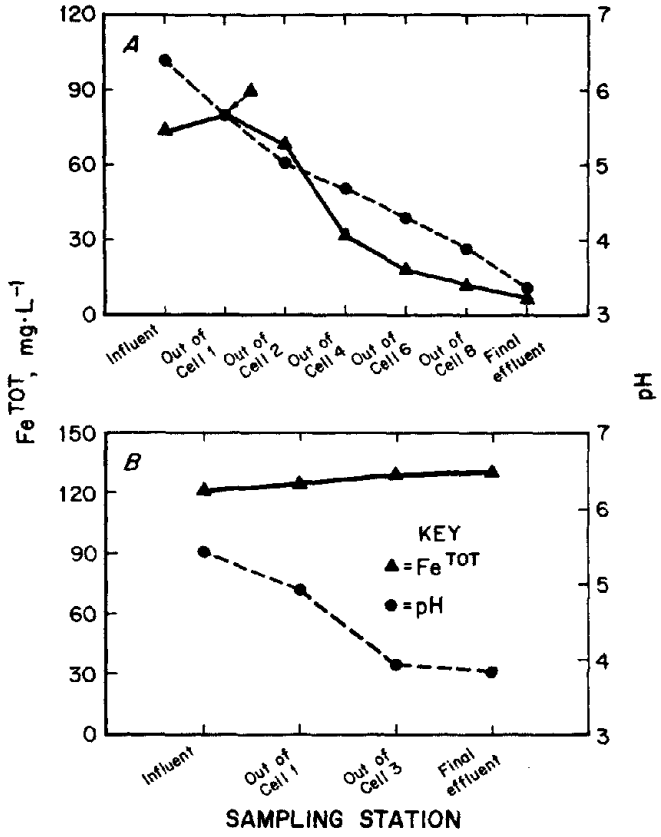

Figure 4.—Concentrations of Fe^{tot} and field pH at two constructed wetlands. *A*, Emlenton wetland; *B*, Cedar Grove wetland.

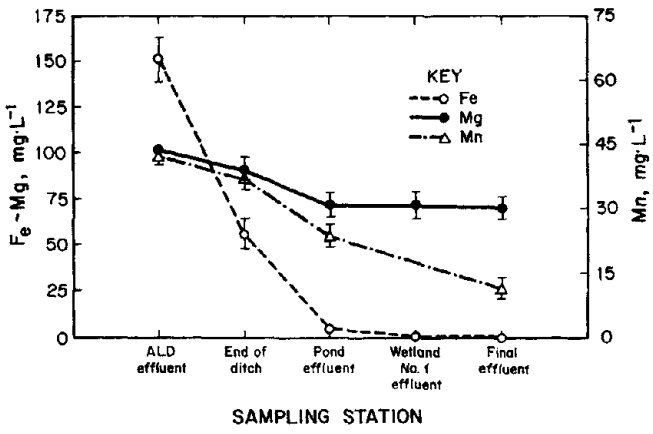

Figure 5.—Mean concentrations of Fe, Mn, and Mg at the Morrison Wetland. Mine water flows linearly from station 1 to station 5. Verticle bars are one standard error of the mean.

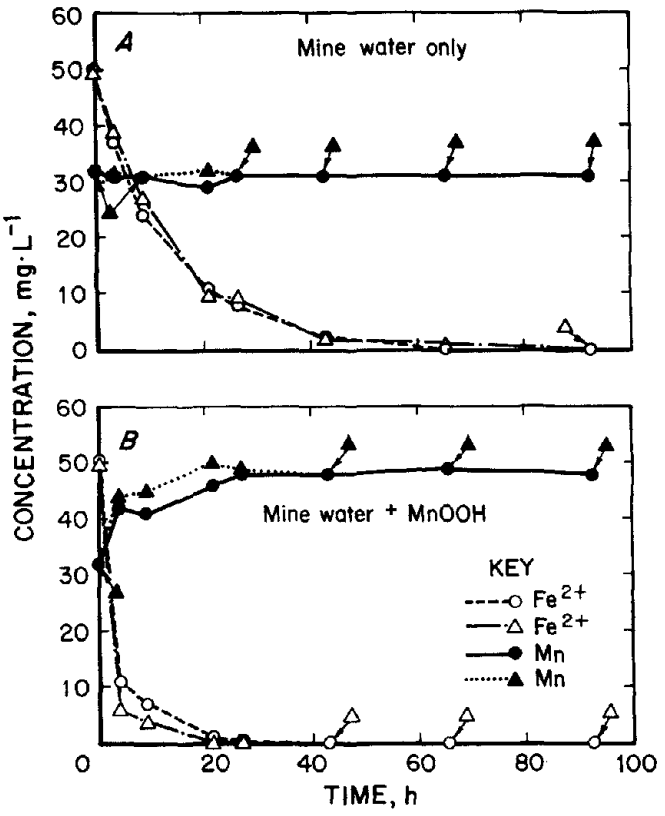

Figure 6.—Changes in concentrations of Fe^{2+} and Mn^{2+}. *A*, absence; *B*, presence of MnOOH. Mine water was collected from influent pipe of Blair wetland. MnOOH was collected from inside of final effluent pipe.

collected from a wetland that removed Fe and Mn in a sequential manner. The wetland influent was alkaline (pH 6.2, 162 mg•L^{-1} alkalinity) and contaminated with 50 mg•L^{-1} Fe and 32 mg•L^{-1} Mn. Two flasks of mine water received MnO_2 additions, while the controls did not receive MnO_2. Concentrations of dissolved Fe and Mn were monitored in each flask over a 73-h period. In all flasks, concentrations of Fe decreased to <1 mg•L^{-1}. In the control flasks, concentrations of Fe decreased to <3 mg•L^{-1} within 43 h. In flasks that received MnO_2, concentrations of Fe decreased to <3 mg•L^{-1} in only 22 h. No change in concentrations of Mn occurred in the control flasks. Concentrations of Mn in the MnO_2 flasks increased by 15 mg•L^{-1} during the first 22 h and did not change during the remaining 50 h of the experiment. The association of accelerated precipitation of Fe with solubilization of Mn^{2+} suggests that the MnO_2 oxidized Fe^{2+} in a manner analogous to reaction K.

The data presented in figures 5 and 6 demonstrate aspects of Fe and Mn chemistry that are important in passive treatment systems. Iron oxidizes and precipitates from alkaline mine water much more rapidly than does Mn. One reason for the differences in kinetics is that the oxidized Mn solids, which are presumed to result from Mn^{2+} oxidation reactions, 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+}, Mn removal is still a very slow process under laboratory conditions. Conditions in a wetland may either accelerate Mn-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 Mn occurs at a much slower rate than does the removal of Fe (empirical evidence for this concept is presented in chapter 3).

MINE WATER CHEMISTRY IN ANAEROBIC ENVIRONMENTS

Chemical and microbial processes in anaerobic environments differ from those observed in aerobic environments. Because O_2 is absent, Fe^{2+} and Mn^{2+} do not oxidize and oxyhydroxide precipitates do not form. Hydroxides of the reduced Fe and Mn ions, $Fe(OH)_2$ and $Mn(OH)_2$, do not form because of their high solubility under acidic or circumneutral conditions. In passive treatment systems where mine water flows through anaerobic environments, its chemistry is affected by chemical and biological processes that generate bicarbonate and hydrogen sulfide.

Limestone Dissolution

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

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

Carbonate dissolution can result in higher concentrations of bicarbonate in anaerobic mine water environments than aerobic environments for two reasons. First, the absence of Fe^{3+} in most anaerobic environments limits the formation of FeOOH coatings that armor carbonate surfaces and inhibit further carbonate dissolution in aerobic environments (*31*). Second, the solubilities of carbonate compounds are directly affected by the partial pressure of dissolved CO_2 (*23-24, 32*). Anaerobic mine water environments commonly contain high CO_2 partial pressures because of the decomposition of organic matter and the neutralization of proton acidity.

The observation that limestone dissolution is enhanced when contact with mine water occurs in an anaerobic environment has resulted in the construction of anaerobic limestone treatment systems. The first demonstration of

this technology was by Turner and McCoy (*15*) 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. After exposure to the atmosphere metal contaminants precipitated from this alkaline discharge much faster than they did from the original acid discharge.

Since Turner and McCoy described their findings in 1990, dozens of additional limestone treatment systems have been constructed (*33-35*). These passive mine water pretreatment systems have become known as anoxic limestone drains or ALD's. In an ALD, mine water is made to flow through a bed of limestone gravel that has been buried to limit inputs of atmospheric oxygen. The containment caused by the burial also traps CO_2 within the treatment system, allowing the development of high CO_2 partial pressures (*36*).

Water quality data from an ALD in western Pennsylvania are shown in table 5 and figure 7. This ALD is a rectangular bed of limestone gravel that is 37 m long by 6 m wide by 1 m deep. The limestone bed is covered with filter fabric and 1 m of clay. No organic matter was incorporated into the limestone system. Water samples were collected from the ALD influent and effluent and at four locations within the ALD. The influent mine water contained high concentrations of ferrous iron and Mn and a small amount of alkalinity. As the mine water flowed through the ALD, pH and concentrations of calcium and alkalinity increased while other measured parameters were unchanged. Between the influent and effluent locations, changes in concentrations of alkalinity (137 $mg \cdot L^{-1}$) and Ca (58 $mg \cdot L^{-1}$) were in stoichiometric agreement with those expected from $CaCO_3$ dissolution.

Table 5.—Chemistry of mine water flowing through the Howe Bridge anoxic limestone drain, January 23, 1992

Parameter	In	Well 1	Well 2	Well 3	Well 4	Eff
pH	5.9	6.1	6.4	6.5	6.5	6.3
Alkalinity	39	75	141	179	183	176
Ca	140	150	183	201	206	198
Fe^{2+}	249	237	246	246	245	244
Fe^{3+}	<1	<1	<1	<1	<1	<1
Mn	34	33	34	34	34	34
Al	<1	<1	<1	<1	<1	<1
Mg	90	87	91	91	90	90
Na	11	11	11	11	11	11
SO_4	1175	1175	1200	1150	1200	1200
CO_2	6.3	4.0	4.7	4.3	4.7	NA

NA Not available.

NOTE.—Water flows linearly from the influent (In) through wells 1, 2, 3, and 4 and out the effluent (Eff). CO_2 values are the partial pressure percentages (atmosphere) of gas samples collected from the headspace within the sampling wells. No gas sample could be collected for the effluent because it is an open pipe.

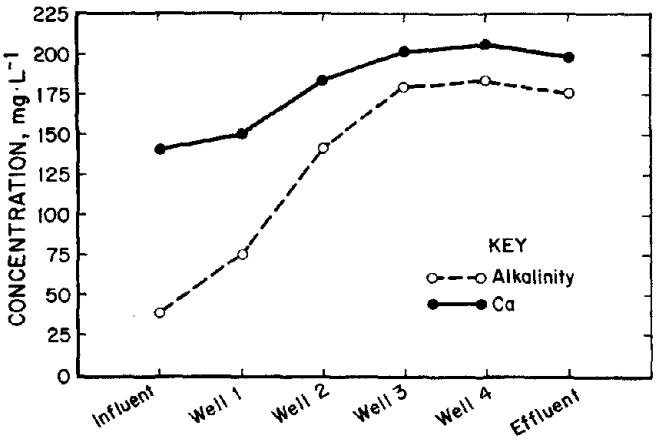

Figure 7.—Concentrations of Ca, and alkalinity for water as it flows through the Howe Bridge ALD. Water flows linearly from influent to effluent.

Dissolution of $CaCO_3$ within the ALD was greater than would be expected from an open system in equilibrium with atmospheric concentrations of CO_2 (0.035%). An equilibrated open system would only produce alkalinity in the range of 50 to 60 $mg \cdot L^{-1}$, and increase Ca concentrations by 4 to 8 $mg \cdot L^{-1}$. Observations of elevated CO_2 gas concentrations within the ALD, and the higher solubility of $CaCO_3$ within the ALD indicate that the ALD acts as a closed system.

Concentrations of alkalinity and Ca changed little between the third well and the ALD effluent. This observation suggests that water within the ALD was already in equilibrium with $CaCO_3$ by the time it reached the third well location. Thus, the amount of alkalinity that can be generated by this ALD is limited to a maximum value that is a function of the CO_2 partial pressures within the ALD. Similar observations of solubility-limited alkalinity generation by an ALD have also been made at a second site in western Pennsylvania (*36*).

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 sink and release hydrogen sulfide and bicarbonate,

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

where CH_2O is used to represent organic matter. Bacterial sulfate reduction is limited to certain environmental

conditions (*37*). The bacteria require the presence of sulfate, suitable concentrations of low-molecular weight carbon compounds, pH >4, and the absence of oxidizing agents such as O_2, Fe^{3+} and Mn^{4+}. These conditions are commonly satisfied in treatment systems that receive coal mine drainage and contain organic matter. High concentrations of sulfate (>200 mg•L^{-1}) 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 Fe or Mn. The low-molecular weight compounds that sulfate-reducing bacteria utilize (lactate, acetate) are common end products of microbial fermentation processes in anoxic environments. The pH requirements can be satisfied by alkalinity generated by microbial activity and carbonate dissolution.

Bacterial sulfate reduction directly affects concentrations of dissolved metals by precipitating them as metal sulfide solids.

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

For Fe, the formation of pyrite is also possible

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

The removal of dissolved metals as sulfide compounds depends on pH, the solubility product of the specific metal sulfide, and the concentrations of the reactants. The solubilities of various metal sulfides are shown in table 6. Laboratory studies have verified that metal removal from mine water subjected to inflows of hydrogen sulfide occurs in an order consistent with the solubility products shown in table 6 (*39*). 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 expected to form only when the concentrations of all other metals in the table are very low (≪1 mg•L^{-1}).

For coal mine drainage, where metal contamination is generally limited to Fe, Mn, and Al, 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.

Table 6.—Solubility products of some metal sulfides

Metal sulfide	*Solubility product*[1]
CdS	1.4×10^{-23}
CuS	4.0×10^{-38}
FeS	1.0×10^{-19}
MnS	5.6×10^{-16}
NiS	3.0×10^{-21}
PbS	1.0×10^{-29}
ZnS	4.5×10^{-24}

[1]See reference 38.

The precipitation of metal sulfides in an organic substrate improves water quality by decreasing the 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% 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 (*40-41*). 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 Fe and Mn oxides, the hydrogen sulfide can be oxidized (table 7). These reactions affect the mineral acidity and the alkalinity in various manners.

Table 7.—Sinks for H_2S in constructed wetlands and their net effect on mine water acidity and alkalinity

Reaction	Effect	
	Acidity[1]	Alkalinity[2]
$H_2S + 2HCO_3^- \rightarrow H_2S(g) + 2HCO_3^-$	0	+100
$H_2S + 2HCO_3^- + Fe^{2+} \rightarrow FeS + 2H_2O + 2CO_2$	-100	0
$H_2S + 2HCO_3^- + 2Fe^{3+} \rightarrow S^0 + 2Fe^{2+} + 2H_2O + 2CO_2$	-100	0
$H_2S + 2HCO_3^- + 2Fe(OH)_3 \rightarrow S^0 + 2Fe^{2+} + 2H_2O + 4OH^- + 2HCO_3^-$	+200	+300
$H_2S + 2HCO_3^- + \frac{1}{2}O_2 \rightarrow S^0 + H_2O + 2HCO_3^-$	0	+100
$H_2S + 2HCO_3^- + FeS + \frac{1}{2}O_2 \rightarrow FeS_2 + H_2O + 2HCO_3^-$	0	+100
$H_2S + 2HCO_3^- + 2O_2 \rightarrow SO_4^{2-} + 2H_2O + 2CO_2$	0	0

[1] Effect based on change in mineral acidity.
[2] Effect based on summed change in bicarbonate and hydroxyl alkalinity.

Table 8 shows the chemistry of surface water and substrate pore water samples collected from a wetland constructed with limestone and spent mushroom compost. Spent mushroom compost consists of a mixture of spoiled hay, horse manure, corn cobs, wood chips, and limestone. At the wetland used in this example, 10 to 15 cm of limestone sand was covered with 20 to 50 cm of compost and planted with cattails. Water flowed through the wetland primarily by surface paths; no efforts were made to force the water through the compost. This design is typical of many compost wetlands constructed in northern Appalachia during the last 10 years. The data shown in table 8 were collected 15 months after the wetland was constructed.

Table 8.—Surface and pore water chemistry at the Latrobe wetland

Parameter	Pore water[1]		Surface water[2]	
	Mean	Std dev	Mean	Std dev
Al	1	5	35	5
Ca	467	188	308	29
Fe^{2+}	215	183	73	39
Fe^{3+}	2	9	24	16
H_2S	37	75	<1	0
Mg	175	48	166	9
Mn	24	10	42	2
Na	11	10	5	1
SO_4	1,674	532	1,967	115
Acidity[3]	493	340	503	86
Alkalinity	885	296	0	0
Net Alkalinity[4]	392	NAp	-503	NAp
pH	6.8	.8	3.1	.1

NAp Not applicable.
Std dev Standard deviation.

[1] A total of 52 water samples were collected on July 25 and August 11, 1988, by the dialysis tube method. Metals were analyzed for every sample. Field pH was measured for 29 samples. Alkalinity was measured for nine samples.

[2] Six samples collected in July and August 1988.

[3] Calculated from pH, Fe^{2+}, Fe^{3+}, Al, Mn, and H_2S for pore water samples and measured by the H_2O_2 method for surface water samples.

[4] Average alkalinity minus average acidity. The nine pore water samples for which alkalinity was measured had a mean net alkalinity of 653 mg/L (std dev = 590).

Surface water at the study site had low pH and high concentrations of Fe, Al, and Mn (table 8). Compared with the surface water, the substrate pore water had higher pH, higher concentrations of alkalinity, ferrous iron, calcium, and hydrogen sulfide, and lower concentrations of sulfate, ferric iron, and aluminum. On average, the pore water had a net alkalinity while the surface water had a net acidity. The alkalinity of the pore water appeared to result from a combination of limestone dissolution and sulfate reduction. The average alkalinity calculated to result from these processes was 703 $mg \cdot L^{-1}$, a value that corresponded reasonably well with the measured difference in acidity, 895 $mg \cdot L^{-1}$.[6]

Compared with surface water, substrate pore water contained elevated concentrations of ferrous iron. High concentrations of Fe^{2+} likely resulted from the dissolution of ferric oxyhydroxides at the redox boundary. FeOOH can be reduced by direct heterotrophic bacterial activity (*42*),

$$CH_2O + 4FeOOH + H_2O \rightarrow 4Fe^{2+} + 8OH^- + CO_2 \quad (Q)$$

and also by H_2S that results from sulfate reduction.

$$H_2S + 2FeOOH \rightarrow 2Fe^{2+} + 4OH^- + S^0 \quad (R)$$

In both cases, the solubilization of ferric hydroxides results in the release of OH^-, which acts to raise pH to circumneutral levels and also reacts with dissolved CO_2 to form bicarbonate. Reduction of ferric hydroxide has no effect on the net acidity of the mine water because the increase in alkalinity is exactly matched by an increase in mineral acidity. If the Fe-enriched pore water diffuses into an aerobic zone, the ferrous iron content should oxidize, hydrolyze, and reprecipitate as ferric oxyhydroxide.

$$4Fe^{2+} + 8OH^- + O_2 \rightarrow 4FeOOH + 2H_2O \quad (S)$$

Because the pore water has circumneutral pH and is strongly buffered by bicarbonate, the removal of iron by oxidation processes from pore water as it diffuses into aerobic surface waters should occur rapidly. Indeed, during the summer months, when the data in table 8 were collected, comparisons of the wetland influent and effluent indicated that the wetland decreased both concentrations of iron and total acidity on every sampling day (figure 8). The decrease in acidity indicates that alkaline pore water was mixing with surface water and neutralizing acidity. The decrease in concentrations of Fe in the surface water indicates that elevated concentrations of Fe^{2+} observed in the pore water were rapidly removed in surface water environments.

ALUMINUM REACTIONS IN MINE WATER

Aluminum has only one oxidation state in aquatic systems, +3. Oxidation and reduction processes, which complicate Fe and Mn chemistry, do not directly affect

[6] The difference between surface and pore water concentrations of sulfate averaged 293 $mg \cdot L^{-1}$, which is equivalent to 305 $mg \cdot L^{-1}$ $CaCO_3$ alkalinity (reaction N); the difference in calcium concentrations averaged 159 $mg \cdot L^{-1}$, which is equivalent to 398 $mg \cdot L^{-1}$ $CaCO_3$ alkalinity (reaction M).

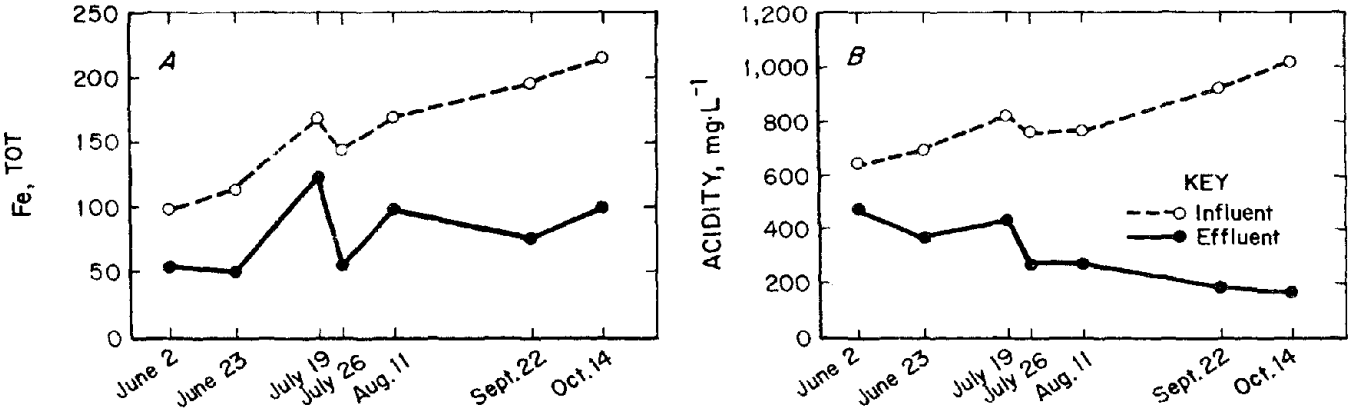

Figure 8.—Influent and effluent concentrations at the Latrobe wetland during the summer of 1988. A, Fe; B, acidity.

concentrations of dissolved Al. Instead, concentrations of Al in mine waters are primarily influenced by the solubility of $Al(OH)_3$ (*23, 43*). At pH levels between 5 and 8, $Al(OH)_3$ is highly insoluble and concentrations of dissolved Al are usually <1 mg•L^{-1}. At pH values <4, $Al(OH)_3$ is highly soluble and concentrations >2 mg•L^{-1} are possible.

The passage of mine water through highly oxidized or highly reduced environments has no effect on concentrations of Al unless the pH also changes. In those cases where the pH of mine water decreases (due to iron oxidation and hydrolysis), concentrations of Al can increase because of the dissolution of alumino-silicate clays by the acidic water. When acidic mine water passes through anaerobic environments, the increased pH that can result from carbonate dissolution or microbial activity causes the precipitation of $Al(OH)_3$.

CHAPTER 3. REMOVAL OF CONTAMINANTS BY PASSIVE TREATMENT SYSTEMS

Chapter 2 described chemical and biological processes that decrease concentrations of mine water contaminants in aquatic environments. The successful utilization of these processes in a mine water treatment system depends, however, on their kinetics. Chemical treatment systems function by creating chemical environments where metal removal processes are very rapid. The rates of chemical and biological processes that underlie passive systems are often slower than their chemical system counterparts and thus require that mine water be retained longer before it can be discharged. Retention time is gained by building large systems such as wetlands. Because the land area available for wetlands on minesites is often limited, the sizing of passive treatment systems is a crucial aspect of their design. Unfortunately, in the past, most passive treatment systems have been sized based on guidelines that ignored water chemistry or on available space, rather than on comparisons of contaminant production by the mine water discharge and expected contaminant removal by the treatment system. Given the absence of quantitative sizing standards, wetlands have been constructed that are both vastly undersized and oversized.

In this chapter, rates of contaminated removal are described for 13 passive treatment systems in western Pennsylvania. The systems were selected to represent the wide diversity of mine water chemical compositions that exist in the eastern United States. The rates that are reported from these sites are the basis of treatment system sizing criteria suggested in chapter 4.

The analytical approach used to quantify the performance of passive treatment systems in this chapter differs from the approach used by other researchers in several respects. First, contaminant removal is evaluated from a rate perspective, not a concentration perspective. Second, changes in contaminant concentrations are partitioned into two components: because of dilution from inputs of freshwater, and because of chemical and biological processes in the wetland. In the evaluations of wetland performance, only the chemical and biological components are considered. Third, treatment systems, or portions of systems, were included in the case studies only if contaminant concentrations were high enough to ensure that contaminant removal rates were not limited by the absence of the contaminant. These unique aspects of the research are discussed in further detail below.

EVALUATION OF TREATMENT SYSTEM PERFORMANCE

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 flow rate of mine water they receive. In the past, concentration efficiency (CE%) has been a common measure of performance (*11-12*). Using iron concentration as an example, the calculation is

$$CE\% = \frac{Fe_{in} - Fe_{eff}}{Fe_{in}} \times 100 \quad (2)$$

where the subscripts "in" and "eff" represent wetland influent and effluent sampling stations and Fe concentrations are in milligram per liter.

Except in carefully controlled environments, CE% is a very poor measure of wetland performance. The efficiency calculation results in the same measure of performance for a system that lowers Fe concentrations from 300 to 100 $mg \cdot L^{-1}$ as one that lowers concentrations from 3 to 1 $mg \cdot L^{-1}$. Neither the flow rate of the drainage nor the size of the treatment system are incorporated into the calculation. As a result, the performances of systems have been compared without accounting for differences in flow rate (which vary from <10 to >1000 $L \cdot min^{-1}$) or for differences in system size (which vary from <0.1 to >10 ha) (*12*).

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 Fe, the calculation is

$$Fe\ (g \cdot d^{-1})_{in} = 1.44 \times flow\ (L \cdot min^{-1}) \times Fe\ (mg \cdot L^{-1})_{in}) \quad (3)$$

where $g \cdot d^{-1}$ is gram per day and 1.44 is the unit conversion factor needed to convert minutes to days and milligrams to grams.

The contaminant load is apportioned to the down flow treatment system by dividing by a measure of the system's size. In this study, treatment systems are sized based on their surface area (SA) measured in square meter,

$$Fe\ (g \cdot m^{-2} \cdot d^{-1})_{in} = Fe\ (g \cdot d^{-1})_{in} / SA. \quad (4)$$

The daily mass of Fe removed by the wetland between two sampling stations, $Fe(g \cdot d^{-1})_{rem}$, is calculated by comparing contaminant loadings at the two points,

$$Fe\ (g \cdot d^{-1})_{rem} = (Fe\ g \cdot d^{-1})_{in} - (Fe\ g \cdot d^{-1})_{eff}. \quad (5)$$

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

$$Fe\ (g \cdot m^{-2} \cdot d^{-1})_{rem} = Fe\ (g \cdot d^{-1})_{rem} / SA. \quad (6)$$

To illustrate the use of contaminant loading and contaminant removal calculations, consider the hypothetical water quality data presented in table 9.

In systems A and B, changes in Fe concentrations are the same (60 $mg \cdot L^{-1}$), but because system B receives four times more flow and thus higher Fe loading, it actually removes four times more Fe from the water. The concentration efficiencies of the two wetlands are equivalent, but the masses of Fe removed are quite different.

Data are shown for system C for three sampling dates on which flow rates and influent iron concentrations vary. On the first date (C1), the wetland removes all of the Fe that it receives. On the next two dates (C2 and C3), Fe loadings are higher and the wetland effluent contains Fe. From an efficiency standpoint, performance is best on the first date and is worst on the third date. From an Fe-removal perspective, the system is removing the least amount of Fe on the first date. On the second and third dates, the wetland removes similar amounts of iron (2,880 and 3,024 $g \cdot d^{-1}$). Variation in effluent chemistry results, not from changes in wetland's Fe-removal performance, but from variation in influent Fe loading.

Table 9.—Hypothetical wetland data and performance evaluations

System	Wetland size, m^2	Flow rate $L \cdot min^{-1}$	Fe Concentration In $mg \cdot L^{-1}$	Fe Concentration Eff $mg \cdot L^{-1}$	Fe Loading In $Kg \cdot d^{-1}$	Fe Loading Eff $Kg \cdot d^{-1}$	Fe removal performance CE %	Fe removal performance Rate $g \cdot m^{-2} \cdot d^{-1}$
A	400	10	100	40	1.4	0.6	60	2.2
B	400	40	100	40	5.8	2.3	60	8.6
C1	500	30	40	<1	1.7	<0.1	99	3.5
C2	500	80	35	10	4.0	1.2	71	5.8
C3	500	150	30	16	6.5	3.5	47	6.0
D	750	50	100	25	7.2	1.8	75	7.2

In Influent.
Eff Effluent.
CE Concentration efficiency.

Lastly, consider a comparison of wetland systems of different sizes. System D removes more iron than any wetland considered (5,400 $g \cdot d^{-1}$), but it is also larger. One would expect that, all other factors being equal, the largest wetland would remove the most Fe. When wetland area is incorporated into the measure by calculating area-adjusted Fe removal rates (gram per square meter per day), System B emerges as the most efficient wetland considered.

DILUTION ADJUSTMENTS

Contaminant concentrations decrease as water flows through treatment systems because chemical and biological processes remove contaminants from solution and because the concentrations are diluted by inputs of freshwater. To recognize and quantify the removal of contaminants by biological and chemical processes in passive treatment systems, it is necessary to remove the effects of dilution. Ideally, studies of treatment systems include the development of detailed hydrologic and chemical budgets so that dilution effects are readily apparent. In practice, the hydrologic information needed to develop these budgets is rarely available, except when systems are built for research purposes. Treatment systems constructed by mining companies and reclamation groups are rarely designed to facilitate flow measurements at all water sampling locations, so estimating dilution from hydrologic information is highly inaccurate or impossible.

An alternative method for distinguishing the effects of dilution from those of chemical and biological processes is through the use of a conservative ion (*44-45*). By definition, the concentration of a conservative ion changes between two sampling points only because of dilution or evaporation. Changes in concentrations of contaminant ions that proportionately exceed those of conservative ions can then be attributed to biological and chemical wetland processes.

In this study, Mg was used as a conservative ion. Magnesium was considered a good indicator of dilution in these systems for both theoretical and empirical reasons. In northern Appalachia, concentrations of Mg in coal mine drainage are often >50 $mg \cdot L^{-1}$, while concentrations in rainfall are <1 $mg \cdot L^{-1}$ and in surface runoff are usually <5 $mg \cdot L^{-1}$. Magnesium is unlikely to precipitate in passive treatment systems because the potential solid precipitates, $MgSO_4$, $MgCO_3$, and $CaMg(CO_3)_2$, do not form at the concentrations and pH conditions found in the systems (*23*). While biological and soil processes exist that may remove Mg in wetlands, their significance is negligible relative to the high Mg loadings that most mine water treatment systems in northern Appalachia receive. The average Mg loading for wetland systems included in this study was ~7,000 g $Mg \cdot m^{-2} \cdot yr^{-1}$. The uptake of dissolved Mg by plants in constructed wetlands can only account for 5 to 10 g $Mg \cdot m^{-2} \cdot yr^{-1}$. This estimate assumes that the net primary productivity of the constructed wetlands is 2,000 $g \cdot m^{-2} \cdot yr^{-1}$ dry weight (*46*) and that the Mg content of this biomass is 0.25% to 0.50% (*47*). The estimate ignores mineralization processes that would decrease the net retention of Mg to lower values. Most constructed wetlands have a clay base that can adsorb Mg by cation exchange processes, but the total removal of Mg by this process is limited to about 100 $g \cdot m^{-2}$. This estimate assumes that the mine water is in contact with a 5-cm-deep clay substrate that has a density of 1.5 $g \cdot cm^{-3}$, a cation exchange capacity of 25 meq per 100 g, and 50% of the available sites are occupied by Mg (*48*). These conservative calculations indicate that less than 2% of the annual Mg loading at the study sites is likely affected by biological and soil processes within the systems.

Empirical data also indicate that Mg is conservative in the wetlands monitored in this study. Table 10 shows influent and effluent concentrations of major noncontaminant ions at eight constructed wetlands. No precipitation had occurred in the study area for 2 weeks previous to collection of the samples, so dilution from rainfall, surface water, or shallow ground water seeps was minimal. Magnesium was the most conservative ion measured. Concentrations of Mg changed by <5% with flow through every wetland, while concentrations of all other ions monitored changed by at least 15% at at least one site.

Table 10.—Influent and effluent concentrations of Ca, Mg, Na, and sulfate at eight constructed wetlands

	Ca			Mg			Na			SO_4		
	In, $mg \cdot L^{-1}$	Eff, $mg \cdot L^{-1}$	Change, %	In, $mg \cdot L^{-1}$	Eff, $mg \cdot L^{-1}$	Change, %	In, $mg \cdot L^{-1}$	Eff, $mg \cdot L^{-1}$	Change, %	In, $mg \cdot L^{-1}$	Eff, $mg \cdot L^{-1}$	Change, %
Donegal	244	241	-1	81	79	-2	6	6	0	729	729	0
Emlenton	429	433	+1	308	306	-1	11	10	-2	2,810	2,770	-1
FH	122	189	+55	51	51	0	5	7	+2	1,125	842	-25
Gourley	117	120	+3	114	117	+3	3	4	+6	1,000	1,030	+3
Latrobe	244	256	+14	127	125	-2	6	11	+8	1,525	1,225	-20
Piney A	416	426	+2	251	262	+4	15	16	+4	2,190	2,120	-3
Piney B	355	354	0	217	216	0	27	27	-2	2,050	2,100	+2
Somerset	307	469	+53	312	312	0	6	7	+15	2,740	2,300	-16

Eff Effluent.
In Influent.
FH Friendship Hill National Historical Site.

Changes in concentrations of Mg were used to adjust for dilution effects by the following method. For each set of water samples from a constructed wetland, a dilution factor (DF) was calculated from changes in concentrations of Mg between the influent and effluent station:

$$DF = Mg_{eff} / Mg_{in}. \quad (7)$$

Contaminant concentrations were adjusted to account for dilution using the DF. When only an influent flow rate was available, the chemical composition of the effluent water sample was adjusted. For Fe, the adjustment calculation was

$$\Delta Fe_{DA} = Fe_{in} - (Fe_{eff} / DF) \quad (8)$$

where ΔFe_{DA} is expressed in milligram per liter. When only an effluent flow rate was available, the chemical composition of the influent water sample was adjusted,

$$\Delta Fe_{DA} = (Fe_{in} \times DF) - Fe_{eff}. \quad (9)$$

Because most of the DF values were <1.00, the adjustment procedures generally resulted in smaller estimates of changes in contaminant concentrations than would have been calculated without the dilution adjustment.

Rates of contaminant removal, expressed as gram per square meter per day, were then calculated from the dilution-adjusted change in concentrations, the flow rate measurement liter per minute, and the SA of the system, in square meter

$$Fe(g \cdot m^{-2} \cdot day^{-1})_{rem} = (\Delta Fe_{DA} \times Flow \times 1.44)/SA. \quad (10)$$

LOADING LIMITATIONS

A primary purpose of this chapter is to define the contaminant removal capabilities of passive treatment systems. Accurate assessments of these capabilities require that the treatment systems studied contain excessive concentrations of the contaminants. A system that is completely effective (lowers a contaminant to <2 $mg \cdot L^{-1}$) may provide an indication that contaminant removal occurs (if dilution is not the cause of concentration changes), but cannot provide an estimate of the capabilities of the removal processes, as the rate of contaminant removal may be limited simply by the contaminant loading rate. For example, in table 9, the removal rate of Fe for wetland C1 is 3.5 $g \cdot m^{-2} \cdot d^{-1}$. This rate is not an accurate estimate of the capability of the wetland to remove Fe because the loading rate on this day was also only 3.5 $g \cdot m^{-2} \cdot d^{-1}$. The data from C1 are not sufficient to estimate whether the wetland could have removed 10 or 100 $g \cdot m^{-2} \cdot d^{-1}$ of Fe. Only when the wetland is overloaded with Fe (days C2 and C3), can the Fe removal capabilities of the wetland be assessed.

The Morrison passive treatment system demonstrates the necessity of recognizing both dilution and loading-limiting situations in the evaluation of the kinetics of metal removal processes. The Morrison system consists of an anoxic limestone drain followed by a ditch, a settling pond, and two wetland cells. Figure 5, previously presented in chapter 2, shows average concentrations of Fe, Mn, and Mg at the sampling stations. Iron loading and removal rates for the sampling stations are shown in table 11. The treatment system decreased concentrations of Fe from 151 $mg \cdot L^{-1}$ at the system influent station (the ALD discharge) to <1 $mg \cdot L^{-1}$ at the final wetland effluent station. Most of the change in Fe chemistry occurred in the ditch, a portion of the system that only accounted for 4% of the total treatment system SA. Calculations of the rate of Fe removal based on the entire treatment system resulted in a value of 1.3 $g \cdot m^{-2} \cdot d^{-1}$. Because this removal rate is equivalent to the load, it does not represent a reliable approximation of the system's Fe-removal capablity. Only when an Fe removal rate is calculated for the ditch, an area where Fe loading exceeded Fe removal, does an accurate assessment of the Fe removal capabilities result.

Table 11.—Average concentrations of Fe, Mn, and Mg at the Morrison passive treatment system

Station	Cumulative area, m^2	Flow, $L \cdot m^{-1}$	Concentration, $mg \cdot L^{-1}$			Removal rate[1], $g \cdot m^{-2} \cdot d^{-1}$	
			Fe	Mn	Mg	Fe	Mn
Influent	0	6.6	151	42	102	NA	NA
Ditch Effluent	43	NA	56	37	91	19.2	0.17
Pond Effluent	461	NA	5	24	72	2.3	0.14
Final Effluent	1,076	NA	<1	71	71	1.3	0.13

NA Not available.
[1]Removal rate based on cumulative area.

Concentrations of Mn at the Morrison effluent station were generally above discharge limits. Manganese was detectable in every effluent water sample (>.4 mg•L^{-1}) and >2 mg•L^{-1} in 75% of the samples. Thus, it was reasonable to evaluate the kinetics of Mn removal based on the SA of the entire treatment system. Concentrations of Mg, however, decreased with flow through the treatment system, suggesting an important dilution component. Effluent water samples contained, on average, 31% lower concentrations of Mg than did the influent samples. On several occassions when the site was sampled in conjunction with a rainstorm, differences between effluent and influent concentrations of Mg were larger than 50%. Measurements of metal removal by the Morrision treatment system that did not attempt to account for dilution would significantly overestimate the actual kinetics of metal removal processes.

Dilution adjustments were possible for every set of water samples collected from a treatment system because concentrations of Mg were determined for every water sample. Problems with loading limitations, however, could not be corrected at every site. At two sites where complete removal of Fe occurred, the Blair and Donegal wetlands, the designs of the systems were not conducive for the establishment of intermediate sampling stations. For these two systems, no Fe removal rates were calculated because complete removal of Fe occurred over an undetermined area of treatment system.

STUDY SITES

The design characteristics of the 13 passive treatment systems monitored during this study are shown in table 12. At four of the sites, acidic mine water was pretreated with anoxic limestone drains (ALD's) before it flowed into constructed wetlands. The construction materials for the wetlands ranged from mineral substances, such as clay and limestone rocks, to organic substances such as spent mushroom compost, manure, and hay bales. Cattails (*Typha latifolia* and, less commonly, *T. angustifolia*) were the most common emergent plants growing in the systems. Three sites contained few emergent plants. Most of the wetland systems consisted of several cells or ponds connected serially. Two systems, however, each consisted of a single long ditch.

The mean influent flow rates of mine drainage at the study sites ranged from 7 to 8,600 L•min^{-1} (table 12). The highest flow rates occurred where drainage discharged from abandoned and flooded underground mines. The lowest flow rates occurred at surface mining sites. Estimated average retention times ranged from 8 h to more than 30 days.

The average chemistry of the influents to the 16 constructed wetlands are shown in table 13. Data from 15 sampling points are shown. At the REM site, two discharges are treated by distinct ALD-wetland systems that eventually merge into a single flow. The combined flows are referred to as REM-Lower. Mine water at the Howe Bridge system is characterized at two locations. The "upper" analysis describes mine water discharging from an ALD that flows into aerobic settling ponds. The "lower" analysis describes the chemistry of water flowing out of the last settling pond and into a large compost-limestone wetland that is constructed so that mine water flows in a subsurface manner.

Table 12.—Construction characteristics of the constructed wetlands

Site	Constructed year	Design	Substrate	Emergent vegetation	SA, m^2	Water depth, cm	Flow rate,[1] L•min^{-1}	Est. ret. time,[2] days
Donegal	1987	Pond, 8 Cells	LS, SMC	*Typha*	8,100	15	501	1.7
Cedar	1989	5 Cells	Clay, LS	. . do.	1,360	15	156	0.9
Keystone	1989	Ditch	Topsoil	None	4,200	100	8,606	.3
Blair	1989	Ditch	Manure, straw	Mixed	1,080	5	11	3.4
Shade	1989	ALD, 2 Cells	LS	None	880	10	10	6.4
Piney	1987	1 Cell	HB	Mixed	2,500	50	468	1.9
Morrison	1990	ALD, 3 Cells	Clay, manure	*Typha*	1,075	30	7	33.9
Emlenton	1987	9 Cells	LS, manure	. . do.	643	50	55	4.1
Somerset	1984	2 Cells	HB, LS, SMC	. . do.	1,005	15	47	2.2
Howe	1991	ALD, 3 Cells	Clay, LS, SMC	None	3,000	50	130	8.0
Latrobe	1987	3 Cells	HB, LS, SMC	*Typha*	2,800	15	86	3.4
REM	1992	2 ALDs, 9 Cells	SMC	. . do.	4,849	30	206	4.9
FH	1988	6 Cells	LS, SMC	. . do.	667	15	15	4.6

Est. Estimated.
FH Friendship Hill National Historical Site.
HB Haybales.
LS Limestone.
ret. Retention.
SA Surface area of wet area.
SMC Spent mushroom compost.
[1] Average values.
[2] Calculated from the water holding capacity and influent flow rate.

Table 13.—Average chemical characteristics of influent water at the constructed wetlands (sites are arranged according to the net acidity)

Site	Number of samples	pH	Composition, mg•L^{-1}						Net Acidity, [1,2] mg•L^{-1}
			Alk	Fe	Mn	Al	Mg	SO_4	
Donegal	29	7.1	202	5	8	<1	81	738	-182
Cedar	26	6.3	336	92	2	<1	54	1,251	-140
Keystone	28	6.3	142	37	<1	<1	14	330	-73
Blair	12	6.2	166	52	30	<1	77	645	-51
Shade	20	6.0	31	<2	22	<1	125	966	-17
Piney	39	5.8	60	1	15	<1	225	1,845	-6
Morrison	34	6.3	271	150	42	<1	102	1,087	75
REM - L	20	6.1	128	190	50	<1	118	1,275	258
Howe - Lower	13	5.6	22	185	34	<1	91	1,128	312
Emlenton	40	4.7	15	89	77	8	249	2,317	320
Somerset	43	4.4	0	162	50	3	193	1,691	373
Howe - Upper	13	6.2	160	272	39	<1	105	1,315	375
REM-Lower	9	3.5	0	246	92	2	171	1,875	496
Latrobe	43	3.5	0	125	32	43	125	1,655	617
REM - R	18	5.5	57	473	130	3	232	2,495	867
FH	73	2.6	0	153	9	58	85	1,733	929

Alk Alkalinity.
FH Friendship Hill National Historical Site.
[1]$CaCO_3$ equivalent.
[2]Negative values indicate alkaline conditions.

Ten of the influents to the constructed wetlands had pH >5 and concentrations of alkalinity >25 mg•L^{-1}. The alkaline character of five of these discharges resulted from pretreatment of the mine water with ALD's. The high concentrations of alkalinity contained by five discharges not pretreated with ALD's arose from natural geochemical reactions within the mine spoil (Donegal and Blair) or the flooded deep mine (Cedar, Keystone, and Piney). For mine waters that contained appreciable alkalinity, the principal contaminants were Fe and Mn.

Concentrations of alkalinity for six of the influents were high enough to result in a net alkaline conditions (negative net acidity in table 13). A seventh alkaline influent, Morrison, was only slightly net acidic. For these seven influents, enough alkalinity existed in the mine waters to offset the mineral acidity associated with Fe oxidation and hydrolysis.

Nine of the influents were highly acidic. Five of the acidic influents contained alkalinity, but mineral acidity associated with dissolved Fe and Mn caused the solutions to be highly net acidic. These inadequately buffered waters were contaminated with Fe and Mn. Four of the waters contained no appreciable alkalinity (pH <4.5) and high concentrations of acidity. Mine waters with low pH were contaminated with Fe, Mn, and Al.

EFFECTS OF TREATMENT SYSTEMS ON CONTAMINANT CONCENTRATIONS

The effects of the treatment systems on contaminant concentrations are shown in table 14. Every system decreased concentrations of Fe. At four sites where the original mine discharge contained elevated concentrations of Fe, the final discharges contained <1 mg•L^{-1}. Nine of the systems decreased Fe concentrations by more than 50 mg•L^{-1}. The largest change in Fe occurred at the Howe Bridge system where concentrations decreased by 197 mg•L^{-1}. From a compliance perspective, the most impressive decrease in Fe occurred at the Morrison system where 151 mg•L^{-1} decreased to <1 mg•L^{-1}.

Fourteen of the passive systems received mine water contaminated with Mn. Eleven of these systems decreased concentrations of Mn. Changes in Mn were smaller than changes in Fe. The largest change in Mn concentration, 31 mg•L^{-1}, occurred at the Morrison site. Only the Donegal treatment system discharged water that consistently met effluent criteria for Mn (<2 mg•L^{-1}). Both the Shade and Blair wetland effluents flowed into settling ponds which discharged water in compliance with regulatory criteria. On occassions, the discharges of the Morrison and Piney treatment systems met compliance criteria.

Every wetland system decreased concentrations of acidity. The Morrison system, which received mine water that contained 75 mg•L^{-1} acidity, always discharged net alkaline water. None of the constructed wetlands that received highly acidic water (net acidity >100 mg•L^{-1}) regularly discharged water with a net alkalinity. During low-flow periods, the Somerset, Latrobe, and FH systems discharged net alkaline water. The largest change in acidity occurred at the Somerset wetland where concentrations decreased by an average 304 mg•L^{-1}.

DILUTION FACTORS

While contaminant concentrations decreased with flow through every constructed wetland, concentrations of Mg also decreased at many of the sites. Decreases in Mg

indicated that part of the improvement in water quality was because of dilution. Average dilution factors for the treatment systems are shown in table 15. For 9 of the 17 systems, average dilution factors were 0.95 to 1.00 and dilution adjustments were minor. At the remaining eight systems, mean DF values were less than 0.95 and dilution adjustments averaged more than 5%. Water quality data from the Morrison and Somerset constructed wetlands were adjusted, on average, by more than 25%.

Dilution factors varied widely between sampling days. Dilution adjustments were higher for pairs of samples collected in conjuction with precipitation events or thaws. Every system was adjusted by more than 5% on at least one occassion (see minimum dilution factors in table 15). Adjustments of more than 20% occurred on at least one occasion at 13 of the 17 study sites.

Few dilution adjustments were >1.00 (see maximum dilution factors in table 15). Of the 390 dilution factors that were calculated for the entire data set, 13 exceeded 1.05. These high dilution factors could have resulted from evaporation or freezing out of uncontaminated water within the treatment system, from temporal changes in water chemistry, or from sampling errors. Most of the high dilution factors were associated with rainstorm events, suggesting temporal changes in water quality. When dilution factors were >1.00, the calculated rates of contaminant removal were greater than would have been estimated without any dilution adjustment. Because of the limited number of sample pairs with high dilution factors, their presence did not markedly affect the average contaminant removal rates for the constructed wetland study areas.

Table 14.—Mean water quality for sampling stations at the constructed wetlands

Site	Sampling station	n[1]	pH	Fe	Mn	Acidity	Mg
Donegal	Pond influent	6	6.4	34	9	NAp	83
	Wetland influent	29	7.1	5	8	NAp	81
	Effluent	28	7.4	<1	2	NAp	80
Cedar	Influent	26	6.3	92	2	NAp	54
	Effluent	27	6.4	41	2	NAp	53
Keystone	Influent	28	6.3	37	1	NAp	14
	Effluent	28	6.4	32	1	NAp	14
Blair	Influent	12	6.2	52	30	NAp	77
	Effluent	8	7.0	<1	5	NAp	59
Shade	LC influent	20	6.0	2	23	NAp	128
	LC effluent	20	6.8	<1	10	NAp	122
Piney	Seep	21	5.4	32	25	NAp	201
	Wetland influent	39	5.8	1	15	NAp	225
	Wetland effluent	39	6.1	<1	11	NAp	225
Morrison	Influent	24	6.3	151	42	75	102
	Ditch	24	6.4	56	37	64	91
	Effluent	24	6.6	<1	11	-1	71
REM-L	Left influent	20	6.1	190	50	258	118
	Left effluent	20	3.8	84	48	225	112
Emlenton	Influent	46	4.7	89	77	320	249
	Effluent	40	3.2	15	73	271	234
Somerset	Influent	43	4.4	162	50	373	193
	Effluent	40	5.5	18	33	69	139
Howe	Influents[2]	13	6.0	265	37	373	101
	Upper effluent	13	5.6	185	34	312	91
	Lower effluent	13	6.2	68	33	112	91
REM-Lower	Influent	9	3.5	246	92	496	171
	Effluent	9	2.9	115	88	436	166
Latrobe	Influent	43	3.5	125	32	617	125
	Cell 3 effluent	43	3.7	56	29	343	122
REM-R	Right influent	18	5.5	473	130	867	232
	Right effluent	18	3.3	338	113	712	201
FH	Influent	73	2.6	153	10	929	85
	Effluent	73	2.9	137	10	674	85

FH Friendship Hill National Historical Site.
LC Limestone cell.
NAp Not applicable.
[1]Number of samples.
[2]The flow-weighted average of two discharges.

Table 15.—Dilution factors for the constructed wetlands

Site	Average	sd	Minimum	Maximum
Donegal	0.99	0.05	0.76	1.04
Cedar	0.99	0.03	0.92	1.05
Keystone	0.99	0.04	0.91	1.15
Blair	0.83	0.10	0.70	1.01
Shade	0.96	0.08	0.76	1.09
Piney	1.00	0.06	0.92	1.31
Morrison Ditch	0.87	0.18	0.40	1.05
Morrison Wetland	0.69	0.25	0.27	1.12
REM-L	0.95	0.09	0.70	1.13
Howe Lower	1.00	0.10	0.80	1.25
Emlenton	0.94	0.09	0.66	1.04
Somerset	0.73	0.30	0.30	1.76
Howe Upper	0.89	0.08	0.73	0.99
REM-Lower	0.93	0.09	0.72	1.01
Latrobe	0.95	0.08	0.75	1.14
REM-R	0.86	0.16	0.36	1.00
FH	1.00	0.12	0.58	1.34

FH Friendship Hill National Historical Site.

REMOVAL OF METALS FROM ALKALINE MINE WATER

Rates of Fe and Mn removal for the study systems are shown in table 16. Significant removal of Fe occurred at every study site. Fe removal rates were directly correlated with pH and the presence of bicarbonate alkalinity (figure 9). These two water quality parameters are closely related because the buffering effect of bicarbonate alkalinity causes mine waters with >50 mg•L alkalinity to typically have a pH between 6.0 and 6.5. Within the group of sites that received alkaline mine water, there was not a significant relationship between the Fe removal rate and the concentration of alkalinity.

Removal of Fe at the alkaline mine water sites appeared to occur principly through the oxidation of ferrous iron and the precipitation of ferric hydroxide (reaction A, chapter 2). Mine water within the systems was turbid with suspended ferric hydroxides. By the cessation of the studies, each of the alkaline water sites had developed thick accumulations of iron oxyhydroxides. Laboratory experiments, discussed in chapter 2, demonstrated that abiotic ferrous iron oxidation processes are rapid in aerated alkaline mine waters. No evidence was found that microbially-mediated anaerobic Fe removal processes, which require the presence of an organic substrate, contributed significantly to Fe removal at the alkaline sites. Fe removal rates at the REM wetlands, which were constructed with fertile compost substrates, did not differ from rates at sites constructed with mineral substrates (Morrison, Howe-Upper, Keystone).

Rates of Fe removal averaged 23 $g \cdot m^{-2} \cdot d^{-1}$ at the six sites that contained alkaline, Fe-contaminated water. Four of the alkaline systems displayed similar rates despite widely varying flow conditions, water chemistry and system designs. The Keystone system, a deep plantless ditch that lowered Fe concentrations in a very large deep mine discharge by 5 mg L^{-1}, removed Fe at a rate of 21 $g \cdot m^{-2} \cdot d^{-1}$. The shallow-water Morrison ditch, which decreased concentrations of Fe in a low-flow seep by almost 100 $mg \cdot L^{-1}$, had an average Fe removal rate of 19 $g \cdot m^{-2} \cdot d^{-1}$. The REM-L and REM-R wetlands, which were constructed almost identically, but received water with contaminant concentrations and flow rates that varied by 200%, displayed Fe removal rates of 20 and 28 $g \cdot m^{-2} \cdot d^{-1}$.

Table 16.—Fe and Mn removal rates at constructed wetland

Site	Fe removal rate				Mn removal rate			
	Mean	Std dev	n	sig?[1]	Mean	Std dev	n	sig?
Donegal	NAp	NAp	NAp	NAp	0.50	0.25	9	yes
Cedar	6.3	2.2	7	yes	0.17	0.41	7	no
Keystone	20.7	5.1	15	yes	NAp	NAp	NAp	NAp
Blair	NAp	NAp	NAp	NAp	0.43	0.37	6	yes
Shade	NAp	NAp	NAp	NAp	0.72	0.64	17	yes
Piney	NAp	NAp	NAp	NAp	1.07	1.34	33	yes
Morrison Dit	19.2	10.6	24	yes	0.17	0.41	24	yes
Morrison Wet	NAp	NAp	NAp	NAp	0.20	0.18	24	yes
REM-L	28.3	5.7	20	yes	-0.05	0.13	20	no
Howe-Lower	8.1	1.9	13	yes	0.06	0.16	13	no
Emlenton	9.1	3.3	39	yes	-0.09	0.19	39	no
Somerset	5.0	4.9	34	yes	-0.01	0.54	34	no
Howe-Upper	42.7	8.2	13	yes	-0.43	0.49	13	no
REM-Lower	12.0	3.4	9	yes	-0.05	0.14	9	no
Latrobe	2.1	1.0	21	yes	0.03	0.09	21	no
REM-R	20.1	4.0	18	yes	0.10	0.33	18	no
FH	0.5	0.5	73	yes	0.00	0.02	73	no

NAp Not applicable.
FH Friendship Hill National Historical Site.
n Sample size.
sig? Significant at 0.05 level.
Std dev Standard deviation.
[1]Yes, rate is significantly greater than zero (t-test); no, rate is not significantly greater than zero (t-test).

Two alkaline mine water sites varied considerably from the other sites in their Fe removal capabilities. The Cedar Grove wetland removed Fe at a rate of 6 $g \cdot m^{-2} \cdot d^{-1}$, while the Howe Bridge Upper site removed Fe at a rate of 43 $g \cdot m^{-2} \cdot d^{-1}$. The Cedar Grove system consists of a series of square cells that may have more short-circuiting flow paths than the rectangular-shaped cells of the other systems. The Cedar Grove system also contains less aeration structures than the other systems. Mine water at the site upwells from a flooded underground mine into a pond that dicharges into a three-cell wetland. Limited topographic relief prevented the inclusion of structures that efficiently aerate the water (i.e., waterfalls, steps). The Howe Bridge Upper system, in contrast, very effectively aerates water. Drainage drops out of a 0.3-m-high pipe, flows down a cascading ditch and through a V-notch weir before it enters a large settling pond. Because the rate of abiotic ferrous iron oxidation is directly proportional to the concentration of dissolved oxygen, insufficient oxygen transfer may explain the low rate of Fe removal at the Cedar Site, while exceptionally good oxygen transfer at the Howe Bridge Upper site may explain its high rate of Fe removal.

At sites where the buffering capacity of bicarbonate alkalinity exceeded the mineral acidity associated with iron hydrolysis, precipitation of Fe did not result in decreased pH. This neutralization was evident at the Morrison, Cedar, Keystone, Blair, Piney, and Donegal sites (table 14). At the Howe Bridge and REM wetlands, the mine water was insufficiently buffered and iron hydrolysis eventually exhausted the alkalinity and pH fell to low levels. The effluents of both REM systems had pH <3.5. The Howe Bridge Upper system discharged marginally alkaline water (<25 $mg \cdot L^{-1}$ alkalinity; pH 5.6). Spot checks of the pH of surface water 20 m into the Howe Bridge Lower wetland (which receives the Upper system effluent) always indicated pH values <3.5.

Significant removal of Mn only occurred at five of the constructed wetlands (table 13). Each of these sites received alkaline mine water (figure 10). Each site also either received water with low concentrations of Fe (Piney and Shade) or developed low concentrations of Fe within the treatment system (Blair, Donegal, and Morrison).

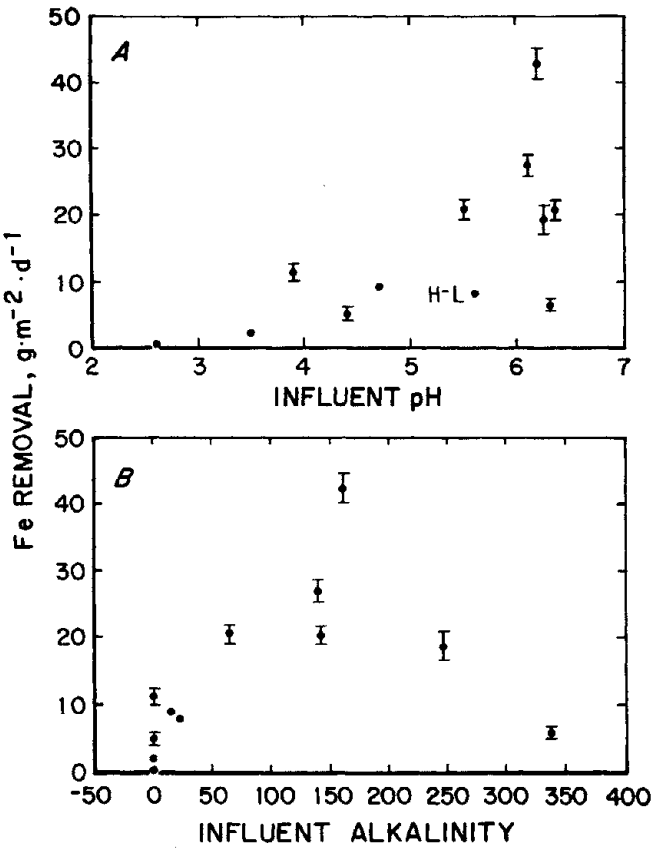

Figure 9.—Relationship between mean Fe removal rates and *A*, mean influent pH and *B*, mean influent alkalinity concentrations. Vertical bars are one standard error above and below the mean. "H-L" is the Howe-Lower site.

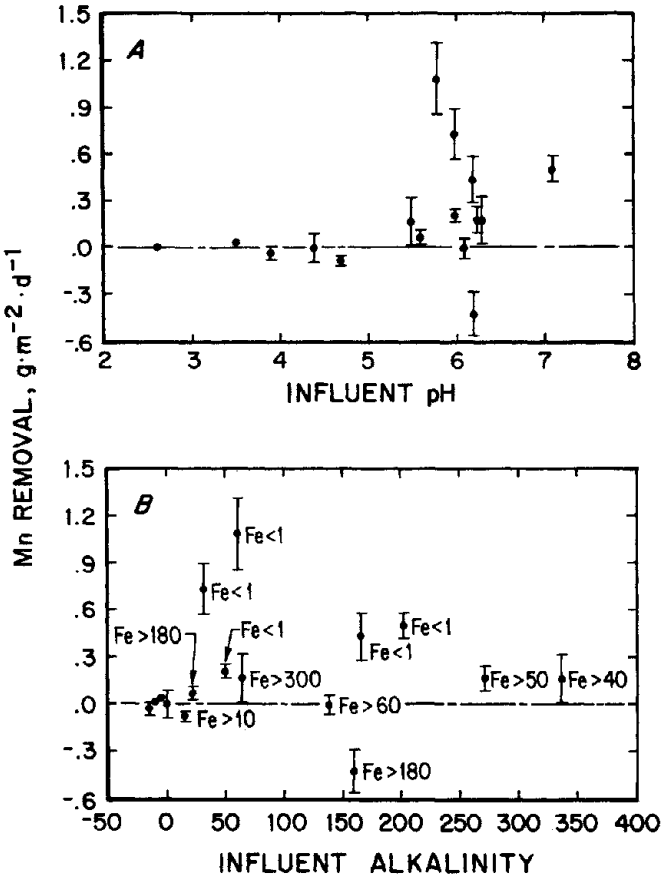

Figure 10.—Relationship between mean Mn removal rates and *A*, mean influent pH and *B*, mean influent alkalinity concentrations. Vertical bars are one standard error above and below mean. Fe values next to the bars are effluent Fe^{2+} values.

Alkaline sites that contained high concentrations of Fe throughout the treatment system (Howe-Upper, REM-L, REM-R, and Cedar), did not remove significant amounts of Mn. The Morrison ditch, which contained water with an average 56 $mg \cdot L^{-1}$ Fe, had a significant Mn removal rate. This rate, however, was derived from an average dilution-adjusted decrease in Mn concentrations of only 1.2 $mg \cdot L^{-1}$ or 3% of the influent concentrations. Because of uncertainities with sampling, analysis, and dilution-adjustment procedures that could reasonably bias Mn data by 2-3%, the authors do not currently place much practical confidence in this value.

The five sites that markedly decreased concentrations of Mn had variable designs. The Donegal wetland has a thick organic and limestone substrate and is densely vegetated with cattails. The Blair and Morrison wetlands contain manure substrates and are densely vegetated with emergent vegetation. The Piney wetland was not constructed with an organic substrate and includes deep open water areas and shallow vegetated areas. The Shade treatment system contains limestone rocks, no organic substrate, and few emergent plants. Thus, chemical aspects of the water, not particular design parameters, appear to principally control Mn removal in constructed wetlands.

The removal of Mn from aerobic mine waters appeared to result from oxidation and hydrolysis processes. Black Mn-rich sediments were visually abundant in the Shade, Donegal, and Blair wetlands. As discussed in chapter 2, the specific mechanism by which these oxidized Mn solids form is unclear. The amorphous nature of the solids prevented identification by standard X-ray diffraction methods. However, samples of Mn-rich solids collected from the Shade and Blair wetlands were readily dissolved by alkaline ferrous iron solutions, indicating the presence of oxidized Mn compounds.

Mn^{2+} can reportedly be removed from water by its sorption to charged FeOOH (ferric oxydroxide) particles (*23, 30*). If this process is occurring at the study wetlands, it is not a significant sink for Mn removal. The bottoms of the Morrison ditch, Howe-Upper, Cedar, REM-L, and REM-R wetlands were covered with precipitated FeOOH and the mine water within these wetlands commonly contained 5 to 10 $mg \cdot L^{-1}$ of suspended FeOOH (difference of the Fe content of unfiltered and filtered water samples). After mine water concentrations were adjusted to reflect dilution, no removal of Mn was indicated at four of the sites and very minor removal of Mn occurred at the fifth site (Morrison ditch).

Although the processes that remove Mn and Fe from alkaline mine water appears to be mechanistically similar (both involve oxidation and hydrolysis reactions), the observed kinetics of the metal removal processes are quite different. In the alkaline mine waters studied, Mn removal rates were 20 to 40 times slower than Fe removal.

The presence or absence of emergent plants in the wetlands did not have a significant effect on rates of either Fe or Mn removal at the alkaline mine water sites. In general, bioaccumulation of metals in plant biomass is an insignificant component of Fe and Mn removal in constructed wetlands (*49*). The ability of emergent plants to oxygenate sediments and the water column (*50*) has been proposed as an important indirect plant function in wetlands constructed to treat polluted water (*51*). Either oxygenation of the water column is not a rate limiting aspect of metal oxidation at the constructed wetlands that received alkaline mine water, or physical oxygen transfer processes are more rapid than plant-induced processes.

REMOVAL OF METALS AND ACIDITY FROM ACID MINE DRAINAGE

Metal removal was slower at constructed wetlands that received acidic mine water than at those that received alkaline mine water. Removal of Mn did not occur at any site that received highly acidic water (figure 10). Removal of Fe occurred at every wetland that received acidic mine water, but the Fe removal rates were less than one-half those determined at alkaline wetlands (figure 9). Because abiotic ferrous iron oxidation processes are extremely slow at pH values <5, virtually all the Fe removal observed at the acidic sites must arise from direct or indirect microbial activity. Microbially-mediated Fe removal under acidic conditions is, however slower than abiotic Fe-removal processes under alkaline conditions.

Wetlands that treat acidic mine water must both precipitate metal contaminants and neutralize acidity. At most wetland sites, acidity neutralization was the slower process. At the Emlenton and REM wetlands, Fe removal processes were accompanied on every sampling occasion by an increase in proton acidity which markedly decreased pH (see figure 4*A*, chapter 2). Mine water pH occasionally decreased with flow through the Latrobe and Somerset wetlands. Thus, for the wetlands included in this study, the limiting aspect of acid mine water treatment was the generation of alkalinity or the removal of acidity (which were considered in this report to be equivalent, see chapter 2). The best measure of the effectiveness of the acid water treatment systems was through the calculation of acidity removal rates.

Acidity can be neutralized in wetlands through the alkalinity-producing processes of carbonate dissolution and bacterial sulfate reduction. As was discussed in chapter 2, the presence of an organic substrate where reduced Eh conditions develop promotes both alkalinity-generating processes. In highly reduced environments where dissolved oxygen and ferric iron are not present, carbonate surfaces are not passivated by FeOOH armoring. Decomposition of the organic substrate can result in elevated

partial pressures of CO_2 and promote carbonate dissolution. The presence of organic matter also promotes the activity of sulfate-reducing bacteria.

The rates of alkalinity generated from these two processes in the constructed wetlands were determined based on dilution-adjusted changes in the concentrations of dissolved Ca and sulfate, the stoichiometry of the alkalinity-generating reactions, and measured flow rates. The calculations are based on the assumption that Ca concentrations only increase because of carbonate dissolution and that sulfate concentrations only decrease because of bacterial sulfate reduction. One possible error in this approach is that sulfate can co-precipitate with ferric hydroxides in low-pH aerobic environments (*52*). The Fe and sulfate content of surface deposits collected from the constructed wetlands indicate that sulfate is incorporated into the precipitates collected from acidic environments at an average Fe:SO_4 ratio of 9.7 (table 17). If all of the Fe removed from mine water is assumed to precipitate as ferric hydroxide with a Fe:SO_4 ratio of 9.7:1, then changes in sulfate concentrations attributable to the co-precipitation process amount to only 5 to 30 $mg \cdot L^{-1}$ at the acid mine water sites. Dilution-adjusted changes in sulfate concentrations at the Somerset, Latrobe, Friendship Hill (FH), and Howe-Lower wetlands were commonly 200 to 500 $mg \cdot L^{-1}$.

Rates of acidity removal, sulfate removal and calcium addition for six constructed wetlands that received acidic mine water are shown in table 18. Significant removal of acidity occurred at all sites. The lowest rates of acidity removal occurred at the Emlenton wetland. This site consists of cattails growing in a manure and limestone substrate. No sulfate reduction was indicated (the rate was not significantly >0). Dissolution of the limestone was indicated, but the rate was the lowest observed.

Table 17.—Fe and SO_4 content of ferric oxyhydroxide deposits; sites are arranged by pH

Site	pH	Composition, ppm dry weight		
		Fe	SO_4	Fe:SO_4
Emlenton	3.0	471,779	64,213	7.4
Latrobe	3.5	288,939	27,991	10.3
Somerset	3.5	461,583	48,263	9.6
Cedar	6.4	362,300	8,946	40.5
Keystone	6.6	398,337	6,888	57.8

[1] Field pH measured where substrate sample collected.

The Latrobe, Somerset, FH, Howe-Lower, and REM systems were each constructed with a spent mushroom compost and limestone substrate. Spent mushroom compost is a good substrate for microbial growth and has a high limestone content (10% dry weight). At these five wetlands, sulfate reduction and limestone dissolution both occurred at significant rates (table 18). The summed amount of alkalinity generated by sulfate reduction and limestone dissolution processes (Reactions M and N, chapter 2) correlated strongly with the measured rate of acidity removal at these four sites ($r > 0.90$ at each site). At the FH wetland, 94% of the measured acidity removal could be explained by these two processes (figure 11).

On average, sulfate reduction and limestone dissolution contributed equally to alkalinity generation at these five sites (51% versus 49%, respectively). The average sulfate removal rate calculated for the compost sites, 5.2 g $SO_4^{-2} \cdot m^{-2} \cdot d^{-1}$, is equivalent to a sulfate reduction rate of ~180 $nmol \cdot cm^{-3} \cdot d^{-1}$. This value is consistent with measurements of sulfate reduction made at the constructed wetlands using isotope methods (*41*) as well as measurements of sulfate reduction made for coastal ecosystems (*53*).

Table 18.—Average rates of acidity removal, sulfate removal, and calcium addition at sites receiving acidic mine water

Site	n	Acidity removal rate			Sulfate removal rate			Calcium addition rate		
		mean	Std dev	sig?[1]	mean	Std dev	sig?	mean	Std dev	sig?
Emlenton	25	3.1	2.4	yes	1.5	5.7	no	0.8	1.21	yes
Somerset	34	9.9	8.6	yes	5.1	5.7	yes	1.7	1.20	yes
Howe Lower	13	15.4	4.1	yes	8.9	7.2	yes	3.9	1.40	yes
REM-Lower	9	7.1	7.2	yes	2.9	2.4	yes	2.6	1.03	yes
Latrobe	21	6.9	4.4	yes	5.9	6.4	yes	0.9	0.07	yes
FH	72	7.0	3.8	yes	3.4	2.6	yes	1.2	0.80	yes

FH Friendship Hill National Historical Site.
n Sample size.
Std dev Standard deviation.
[1]Yes, rate is significantly greater than zero (t-test); no, rate is not significantly greater than zero (t-test).

The highest rates of acidity removal, sulfate reduction, and limestone dissolution all occurred at the Howe-Lower site. This system differs from the others by its subsurface flow system. Drainage pipes, buried in the limestone that underlies the compost, cause the mine water to flow directly through the substrate. At the Somerset, Latrobe, REM, and FH systems, water flows surficially through the wetlands. Mixing of the acidic surface water and alkaline substrate waters presumably occurs by diffusion processes at the surface-flow sites. By directly contacting contaminated water and alkaline substrate, the Howe-Lower site is extracting alkalinity from the substrate at a significantly higher rate than occurs in surface flow systems. How long the Howe-Upper system can continue to generate alkalinity at the present rates is unknown. Monitoring of the system, currently in its third year of operation, is continuing.

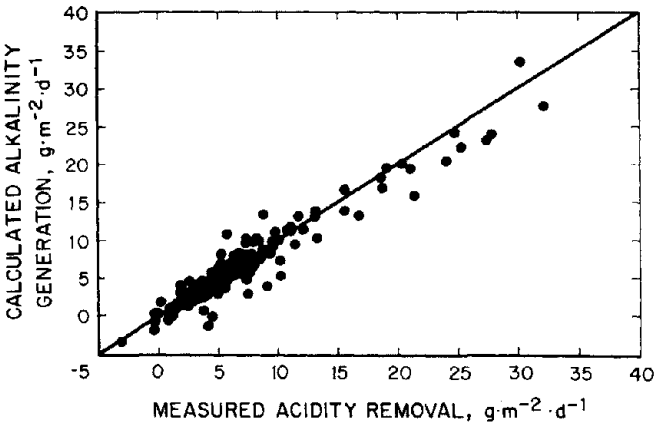

Figure 11.—Measured rates of alkalinity generation and acidity removal at the Friendship Hill wetland. Units are $g \cdot m^{-2} \cdot d^{-1}$ $CaCO_3$ equivalent.

CHAPTER 4. DESIGN AND SIZING OF PASSIVE TREATMENT SYSTEMS

Three principal types of passive technologies currently exist for the treatment of coal mine drainage: aerobic wetland systems, wetlands that contain an organic substrate, and anoxic limestone drains. In aerobic wetland systems, oxidation reactions occur and metals precipitate primarily as oxides and hydroxides. Most aerobic wetlands contain cattails growing in a clay or spoil substrate. However, plantless systems have also been constructed and at least in the case of alkaline influent water, function similarly to those containing plants (chapter 3).

Wetlands that contain an organic substrate are similar to aerobic wetlands in form, but also contain a thick layer of organic substrate. This substrate promotes chemical and microbial processes that generate alkalinity and neutralize acidic components of mine drainage. The term "compost wetland" is often used in this report to describe any constructed wetland that contains an organic substrate in which biological alkalinity-generating processes occur. Typical substrates used in these wetlands include spent mushroom compost, *Sphagnum* peat, haybales, and manure.

The ALD is a buried bed of limestone that is intended to add alkalinity to the mine water (*15, 33-34*). The limestone and mine water are kept anoxic so that dissolution can occur without armoring of limestone by ferric oxyhydroxides. ALD's are only intended to generate alkalinity, and must be followed by an aerobic system in which metals are removed through oxidation and hydrolysis reactions.

Each of the three passive technologies is most appropriate for a particular type of mine water problem. Often, they are most effectively used in combination with each other. In this chapter, a model is presented that is useful in deciding whether a mine water problem is suited to passive treatment, and also, in designing effective passive treatment systems.

Two sets of sizing criteria are provided (table 19). The "abandoned mined land (AML) criteria" are intended for groups that are attempting to cost-effectively decrease contaminant concentrations. In many AML situations, 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 (chapter 3). Most of the removal rates were measured for treatment systems (or parts of treatment systems) that did not consistently lower concentrations of contaminants to compliance with OSM effluent standards. In particular, the Fe sizing factor for alkaline mine water ($20\ g \cdot m^{-2} \cdot d^{-1}$) is based on data from six sites, only one of which lowers Fe concentrations to compliance.

Table 19.—Recommended sizing for passive treatment systems

	AML criteria, $g \cdot m^{-2} \cdot d^{-1}$		Compliance criteria, $g \cdot m^{-2} \cdot d^{-1}$	
	Alkaline	Acid	Alkaline	Acid
Fe	20	NAp	10	NAp
Mn	1.0	NAp	0.5	NAp
Acidity ..	NAp	7	NAp	3.5

NAp Not applicable.

It is possible that Fe removal rates are a function of Fe concentration; i.e., as concentrations get lower, the size of

system necessary to remove a unit of Fe contamination (e.g., 1 $g \cdot d^{-1}$) gets larger. To account for this possibility, a more conservative sizing value for systems where the effluent must meet regulatory guidelines was provided (table 1). These are referred to as "compliance criteria." The sizing value for Fe, 10 $g \cdot m^{-2} \cdot d^{-1}$, is in agreement with the findings of Stark (*17*) for a constructed compost wetland in Ohio that receives marginally acidic water. This rate is larger, by a factor of 2, than the Fe removal rate reported by Brodie (*18*) for aerobic systems in southern Appalachia that are regularly in compliance.

The Mn removal rate used for compliance, 0.5 $g \cdot m^{-2} \cdot d^{-1}$, is based on the performance of five treatment systems, three of which consistently lower Mn concentrations to compliance levels. A higher removal value, 1 $g \cdot m^{-2} \cdot d^{-1}$, is suggested for AML sites. Because the toxic effects of Mn at moderate concentrations (<50 $mg \cdot L^{-1}$) are generally not significant, except in very soft water (*54*), and the size of wetland necessary to treat Mn-contaminated water is so large, AML sites with Fe problems should receive a higher priority than those with only Mn problems.

The acidity removal rate presented for compost wetlands is influenced by seasonal variations that cannot currently be corrected with wetland design (*55*). This is not a problem for mildly acidic water, where the wetland can be sized in accordance with winter performance, nor should it be a major problem in warmer climates. In northern Appalachia, however, no compost wetland that consistently transforms highly acidic water (>300 $mg \cdot L^{-1}$ acidity) into alkaline water is known. One of the study sites, which receives water with an average of 600 $mg \cdot L^{-1}$ acidity and does not need to meet a Mn standard, has discharged water that only required chemical treatment during winter months. While considerable cost savings are realized at the site because of the compost wetland, the passive system must be supported by conventional treatment during a portion of the year.

Because long-term metal-removal capabilities of passive treatment systems are currently uncertain, current Federal regulations require that the capability for chemical treatment exist at all bonded sites. This provision is usually met by placing a "polishing pond" after the passive treatment system. The design and sizing model does not currently account for such a polishing pond.

All passive treatment systems constructed at active sites need not be sized according to the compliance criteria provided in table 19. Sizing becomes a question of balancing available space and system construction costs versus influent water quality and chemical treatment costs. Mine water can be treated passively before the water enters a chemical treatment system to reduce water treatment costs or as a potential part-time alternative to full-time chemical treatment. In those cases where both passive and chemical treatment methodologies are utilized, many operators find that they recoup the cost of the passive treatment system in less than a year by using simpler, less expensive chemical treatment systems and/or by decreasing the amount of chemicals used.

A flow chart that summarizes the design and sizing model is shown in figure 12. The model uses mine drainage chemistry to determine system design, and contaminant loadings combined with the expected removal rates in table 19 to define system size. The following text details the use of this flow chart and also discusses aspects of the model that are currently under investigation.

CHARACTERIZATION OF MINE DRAINAGE DISCHARGES

To design and construct an effluent treatment system, the mine water must be characterized. An accurate measurement of the flow rate of the mine discharge or seep is required. Water samples should be collected at the discharge or seepage point for chemical analysis. Initial water analyses should include pH, alkalinity, Fe, Mn, and hot acidity (H_2O_2 method) measurements. If an anoxic limestone drain is being considered, the acidified sample should be analyzed for Fe^{3+} and Al, and a field measurement of dissolved oxygen should be made.

Both the flow rate and chemical composition of a discharge can vary seasonally and in response to storm

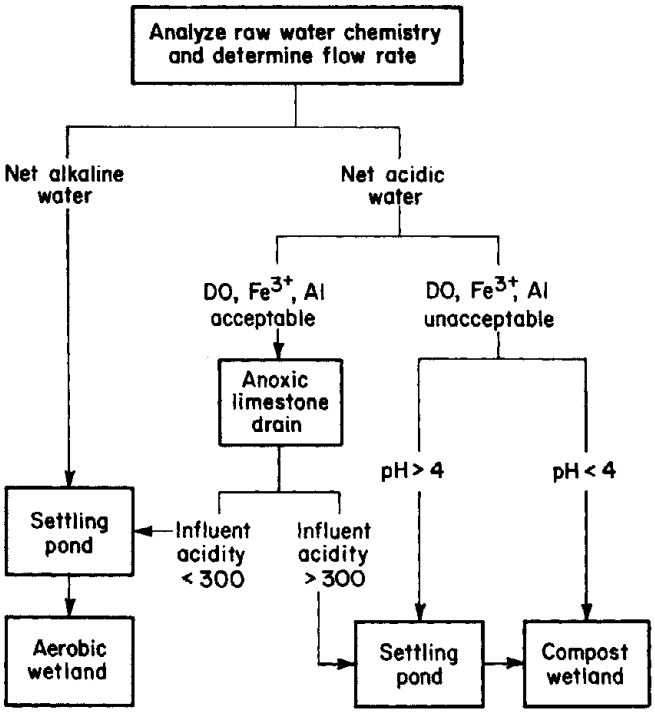

Figure 12.—Flow chart showing chemical determinations necessary for the design of passive treatment systems.

events. If the passive treatment system is expected to be operative during all weather conditions, then the discharge flow rates and water quality should be measured in different seasons and under representative weather conditions.

CALCULATIONS OF CONTAMINANT LOADINGS

The size of the passive treatment system depends on the loading rate of contaminants. Calculate contaminant (Fe, Mn, acidity) loads by multiplying contaminant concentrations by the flow rate. If the concentrations are milligrams per liter and flow rates are liters per minute, the calculation is

$$[\text{Fe,Mn,Acidity}]\ \text{g} \cdot \text{d}^{-1} = \text{flow} \times [\text{Fe,Mn,Acidity}] \times 1.44 \quad (11)$$

If the concentrations are milligrams per liter and flow rates are gallons per minute, the calculation is

$$[\text{Fe,Mn,Acidity}]\ \text{g} \cdot \text{d}^{-1} = \text{flow} \times [\text{Fe,Mn,Acidity}] \times 5.45 \quad (12)$$

Calculate loadings for average data and for those days when flows and contaminant concentrations are highest.

CLASSIFICATION OF DISCHARGES

The design of the passive treatment system depends largely on whether the mine water is acidic or alkaline. One can classify the water by comparing concentrations of acidity and alkalinity.

Net Alkaline Water: alkalinity > acidity
Net Acidic Water: acidity > alkalinity

The successful treatment of mine waters with net acidities of 0 to 100 $mg \cdot L^{-1}$ using aerobic wetlands has been documented in this report and elsewhere (*14, 18*). In these systems, alkalinity either enters the treatment system with diluting water or alkalinity is generated within the system by undetermined processes. Currently, there is no method to predict which of these marginally acidic waters can be treated successfully with an aerobic system only. For waters with a net acidity >0, the incorporation of alkalinity-generating features (either an ALD or a compost wetland) is appropriate.

PASSIVE TREATMENT OF NET ALKALINE WATER

Net alkaline water contains enough alkalinity to buffer the acidity produced by metal hydrolysis reactions. The metal contaminants (Fe and Mn) 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 Fe appears to be limited by dissolved O_2 concentrations. Standard features that can aerate the drainage, such as waterfalls or steps, should be followed by quiescent areas. Aeration only provides enough dissolved O_2 to oxidize about 50 $mg \cdot L^{-1}$ Fe^{2+}. Mine drainage with higher concentrations of Fe^{2+} will require a series of aeration structures and wetland basins. The wetland cells allow time for Fe oxidation and hydrolysis to occur and space in which the Fe floc can settle out of suspension. The entire system can be sized based on the Fe removal rates shown in table 19. For example, a system being designed to improve water quality on an AML site should be sized by the following calculation:

$$\text{Minimum wetland size } (\text{m}^2) = \text{Fe loading } (\text{g} \cdot \text{d}^{-1}) / 20\ (\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}). \quad (13)$$

If Mn removal is desired, size the system based on the Mn removal rates in table 19. Removal of Fe and Mn occurs sequentially in passive systems. If both Fe and Mn removal are necessary, add the two wetland sizes together.

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

Often, several wetland cells are connected by flow through a V-notch weir, lined railroad tie steps, or down a ditch. 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, lined with nonbiodegradable erosion control fabric, and coarse rip rap if high flows are expected (*18*). Proper spillway design can preclude future maintenance costs because of 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 polyvinyl chloride (PVC). More details on the construction of aerobic wetland systems can be found in a text by Hammer (*56*).

The geometry of the wetland site as well as flow control and water treatment considerations may dictate the

use of multiple wetland cells. The intercell connections may also serve as aeration devices. If there are elevation differences between the cells, the interconnection should dissipate kinetic energy and be designed to avoid erosion and/or the mobilization of precipitates.

It is recommended that the freeboard of aerobic wetlands constructed for the removal of Fe be at least 1 m. Observations of sludge accumulation in existing wetlands suggest that a 1-m freeboard should be adequate to contain 20 to 25 years of FeOOH accumulation.

The floor of the wetland cell may be sloped up to about 3% 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 in chapter 3, some of the aerobic systems that have been constructed to treat alkaline mine water have little emergent plant growth. Metal removal rates in these plantless, aerobic systems appears to be similar to what is observed in aerobic systems containing plants. However, plants may provide values that are 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.

PASSIVE TREATMENT OF NET ACID WATER

Treatment of acidic mine water requires the generation of enough alkalinity to neutralize the excess acidity. Currently, there are two passive methods for generating alkalinity: construction of a compost wetland or pretreatment of acidic drainage by use of an ALD. In some cases, the combination of an ALD and a compost wetland may be necessary to treat the mine water.

ALD's produce alkalinity at a lower cost than do compost wetlands. However, not all water is suitable for pretreatment with ALD's. The primary chemical factors believed to limit the utility of ALD's are the presence of ferric iron (Fe^{3+}), aluminum (Al) and dissolved oxygen (DO). When acidic water containing any Fe^{3+} or Al contacts limestone, metal hydroxide particulates (FeOOH or $Al(OH)_3$) will form. No oxygen is necessary. Ferric hydroxide can armor the limestone, limiting its further dissolution. Whether aluminum hydroxides armor limestone has not been determined. 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 within the ALD, and thus potentially cause armoring and plugging. While the short-term performance of ALD's that receive water containing elevated levels of Fe^{3+}, Al, or DO can be spectacular (total removal of the metals within the ALD) (*34*), the long-term performance of these ALD's is questionable.

Mine water that contains very low concentrations of DO, Fe^{3+} and Al (all <1 mg•L^{-1}) is ideally suited for pretreatment with an ALD. As concentrations of these parameters rise above 1 mg•L^{-1}, the risk that the ALD will fail prematurely also increases. Recently, two ALD's constructed to treat mine water that contained 20 mg•L^{-1} Al became plugged after 6-8 months of operation.

In some cases, the suitability of mine water for pretreatment with an ALD can be evaluated based on the type of discharge and measurements of field pH. Mine waters that seep from spoils and flooded underground mines and have a field pH >5 characteristically have concentrations of DO, Fe^{3+}, and Al that are all <1 mg•L^{-1}. Such sites are generally good candidates for pretreatment with an ALD. Mine waters that discharge from open drift mines or have pH <5 must be analyzed for Fe^{3+} and Al. Mine waters with pH <5 can contain dissolved Al; mine waters with pH <3.5 can contain Fe^{3+}. In northern Appalachia, most mine drainages that have pH <3 contain high concentrations of Fe^{3+} and Al.

PRETREATMENT OF ACIDIC WATER WITH ALD

In an ALD, alkalinity is produced when the acidic water contacts the limestone in an anoxic, closed environment. It is important to use limestone with a high $CaCO_3$ content because of its higher reactivity compared with a limestone with a high $MgCO_3$ or $CaMg(CO_3)_2$ content. The limestones used in most successful ALD's have 80% to 95% $CaCO_3$ content. Most effective systems have used number 3 or 4 (baseball-size) limestone. Some systems constructed with limestone fines and small gravel have failed, apparently because of plugging problems. The ALD must be sealed so that inputs of atmospheric oxygen are minimized and the accumulation of CO_2 within the ALD is maximized. This is usually accomplished by burying the ALD under several feet of clay. Plastic is commonly placed between the limestone and clay as an additional gas barrier. In some cases, the ALD has been completely wrapped in plastic before burial (*35*). The ALD should be designed so that the limestone is inundated 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 ALD's vary considerably. Most older ALD's were constructed as long narrow drains, approximately 0.6 to 1.0 m wide. A longitudinal section and cross section of such an ALD is shown in figure 13. The ALD shown was constructed in October 1990, and is 1 m wide, 46 m long and contains about 1 m depth of number 4 limestone. The limestone was covered with two layers of 5 mil plastic, which in turn was covered with

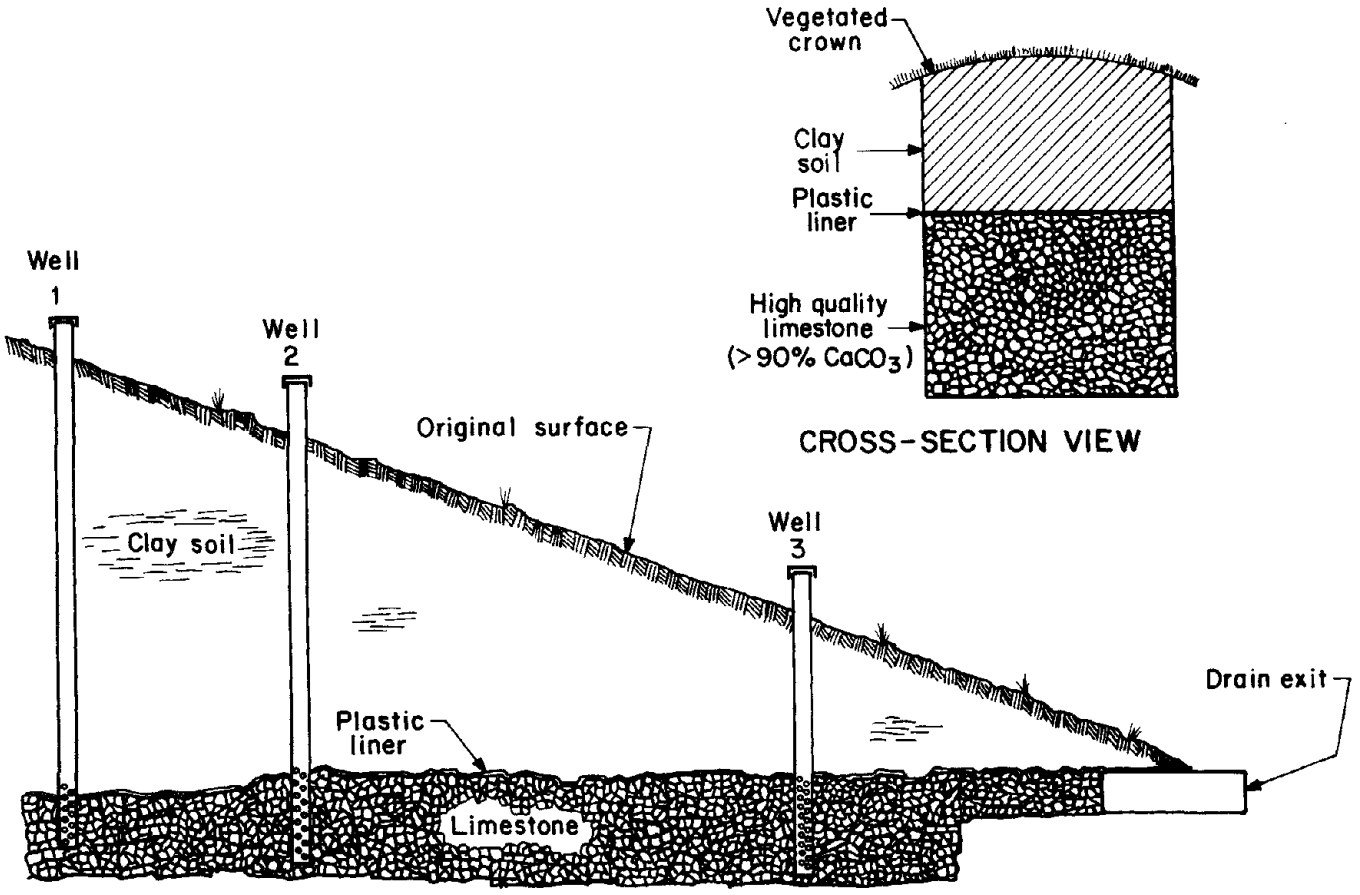

Figure 13.—Longitudinal-section and cross-section of the Morrison ALD. Wells are for sampling purposes and have no importance to drain's functioning.

0.3 to 3 m of on-site clay to restore the original surface topography (*34, 36*).

At sites where linear ALD's are not possible, anoxic limestone beds have been constructed that are 10 to 20 m wide. These bed systems have produced alkalinity concentrations similar to those produced by the more conventional drain systems.

The mass of limestone required to neutralize a certain discharge for a specified period can be readily calculated from the mine water flow rate and assumptions about the ALD's alkalinity-generating performance. Recent USBM research indicates that approximately 14 h of contact time between mine water and limestone in an ALD is necessary to achieve a maximum concentration of alkalinity (*57*). To achieve 14 h of contact time within an ALD, ~3,000 kg of limestone rock is required for each liter per minute of mine water flow. An ALD that produces 275 $mg \cdot L^{-1}$ of alkalinity (the maximum sustained concentration thus far observed for an ALD), dissolves ~1,600 kg of limestone a decade per each liter per minute of mine water flow. To construct an ALD that contains sufficient limestone to insure a 14-h retention time throughout a 30-yr period, the limestone bed should contain ~7,800 kg of limestone for each liter per minute of flow. This is equivalent to 30 tons of limestone for each gallon per minute of flow. The calculation assumes that the ALD is constructed with 90% $CaCO_3$ limestone rock that has a porosity of 50%. The calculation also assumes that the original mine water does not contain ferric iron or aluminum. The presence of these ions would result in potential problems with armoring and plugging, as previously discussed.

Because the oldest ALD's are only 3 to 4 yr old, it is difficult to assess how realistic these theoretical calculations are. Questions about the ability of ALD's to maintain unchannelized flow for a prolonged period, whether 100% of the $CaCO_3$ content of the limestone can be expected to dissolve, whether the ALD's 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 $mg \cdot L^{-1}$) might eventually result in armoring of the limestone with ferric hydroxides, have not yet been addressed.

The anoxic limestone drain is one component of a passive treatment system. When the ALD operates ideally, its only effect on mine water chemistry is to raise pH to

circumneutral levels and increase concentrations of calcium and alkalinity. Dissolved Fe^{2+} and Mn 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 then be treated with a settling basin and an aerobic 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 settling 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 acidities <150 mg$\cdot$L^{-1} are readily treated with an ALD and aerobic wetland system.

If the mine water is contaminated with only Fe^{2+} and Mn, and the acidity exceeds 300 mg$\cdot$L^{-1}, it is unlikely that an ALD constructed using current practices will dis-charge net alkaline water. When this partially neutralized water is treated aerobically, the Fe will precipitate rapidly, but the absence of sufficient bufferring 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 DO content of water flowing out of aerobic systems. If the treatment goal is to neutralize all of the acidity passively, then a compost wetland should be built so that additional alkalinity can be generated. Such a treatment system thus contains all three passive technologies. The mine water flows through an ALD, into a settling pond and an aerobic system, and then into a compost wetland.

If the mine water is contaminated with ferric iron (Fe^{3+}) or Al, higher concentrations of acidity can be treated with an ALD than when the water is contaminated with only Fe^{2+} and Mn. This enhanced performance results from a decrease in mineral acidity because of the hydrolysis and precipitation of Fe^{3+} and Al within the ALD. These metal-removing reactions decrease the mineral acidity of the water. ALD's constructed to treat mine water contaminated with Fe^{3+} and Al and having acidities greater than 1,000 mg$\cdot$L^{-1} have discharged net alkaline water. The long-term prognosis for these metal-retaining systems has been questioned (*34*). However, even if calculations of system longevity (as described above) are inaccurate for waters contaminated with Fe^{3+} and Al, their treatment with an ALD may turn out to be cost-effective when compared with chemical alternatives (*35*).

When a mine water is contaminated with Fe^{2+} and Mn and has an acidity betweem 150 and 300 mg$\cdot$L^{-1}, 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 is dependent on chemical characteristics of the acid mine water. An experimental method has been developed that results in an accurate assessment of the amount of alkalinity that will be generated when a particular mine water contacts a particular limestone (*58*). The method involves the anoxic incubation of the mine water in a container filled with limestone gravel. In experiments at two sites, the concentration of alkalinity that developed in these containers after 48 h correlated well with the concentrations of alkalinity measured in the ALD effluents at both sites.

TREATING MINE WATER WITH COMPOST WETLAND

When mine water contains DO, Fe^{3+} or Al, or contains concentrations of acidity >300 mg$\cdot$L^{-1}, construction of a compost wetland is recommended. Compost wetlands generate alkalinity through a combination of bacterial activity and limestone dissolution. The desired sulfate-reducing bacteria require a rich organic substrate in which anoxic conditions will 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% 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 metric ton of compost will cover about 3.5 m^2 to a depth of 45 cm thick. This is equivalent to one ton per 3.5 yd^2. 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 well into the substrate prior to flooding the wetland cell.

Compost wetlands in which water flows on the surface of the compost remove acidity (e.g., generate alkalinity) at rates of approximately 2-12 g$\cdot$m$^{-2}\cdot$d^{-1}. This range in performance is largely a result of seasonal variation: lower rates of acidity removal occur in winter than in summer (*55*). Research in progress indicates that supplementing the compost with limestone and incorporating system designs that cause most of the water to flow through the

compost (as opposed to on the surface) may result in higher rates of limestone dissolution and better winter performance.

Compost wetlands should be sized based on the removal rates in table 19. For an AML site, the calculation is

$$\text{Minimum Wetland Size } (m^2) = \text{Acidity Loading } (g \cdot d^{-1}/7). \quad (14)$$

In many wetland systems, the compost cells are preceded with a single aerobic pond in which Fe oxidation and precipitation occur. This feature is useful where the influent to the wetland is of circumneutral pH (either naturally or because of pretreatment with an ALD), and rapid, significant removal of Fe is expected as soon as the mine water is aerated. Aerobic ponds are not useful when the water entering the wetland system has a pH <4. At such low pH, Fe oxidation and precipitation reactions are quite slow and significant removal of Fe in the aerobic pond would not be expected.

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 dike and spillway stability. 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 will uproot significant amounts of cattails and other aquatic vegetation. Muskrats can be discouraged by lining dike inslopes with chainlink fence or riprap to prevent burrowing (*13*). Beavers cause water level disruptions because of damming and also 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° elbows on the upstream end have been used as discharge structures in beaver-prone areas (*18*). Otherwise, shallow ponds with dikes with shallow slopes toward wide, riprapped spillways may be the best design for a beaver-infested system.

Mosquitos can be a problem where mine water is alkaline. In southern Appalachia, mosquitofish (*Gambusia affinis*) have been introduced into alkaline-water wetlands. Other insects, such as the armyworm, have devastated monocultural wetlands with their appetite for cattails (*59*). The use of a variety of plants in a system will minimize such problems.

CHAPTER 5. SUMMARY AND CONCLUSIONS

The treatment of contaminated coal mine drainage requires the precipitation of metal contaminants and the neutralization of acidity. In conventional treatment systems, distinctions between these two treatment objectives are blurred by additions of highly basic chemicals that simultaneously cause the rapid precipitation of metal contaminants and the neutralization of acidity. Passive treatment differs from conventional treatment by its distinction between these two treatment objectives. It is possible to passively precipitate Fe contaminants from mine water, but have little effect on the mine water acidity. Alternatively, it is possible to passively add neutralizing capacity to acidic mine water without decreasing metal concentrations.

Waters that contain high concentrations of bicarbonate alkalinity are most amenable to treatment with constructed wetlands. Bicarbonate acts as a buffer that neutralizes the acidity produced when Fe and Mn precipitate and maintains a pH between 5.5 and 6.5. At this circumneutral pH, Fe and Mn precipitation processes are more rapid than under acidic pH conditions. Given the ability of bicarbonate alkalinity to positively impact both the metal precipitation and neutralization aspects of mine water treatment, it is not surprising that the most noteworthy applications of passive treatment have been at sites where the mine water was net alkaline. The most successful wetlands constructed in western Pennsylvania in the early 1980's treated mine waters that contained alkalinity. All of the early successes of the TVA were, likewise, with waters that were alkaline (*13*). Similarly, the Simco wetland in Ohio, which has discharged compliance water for several years (*17*), receives water containing ~160 $mg \cdot L^{-1}$ alkalinity. In this study, the two treatment systems that met all effluent discharge requirements (Donegal and Blair) both received alkaline, metal-contaminated water.

When mine water is acidic, enough alkalinity must be generated by the passive treatment system to neutralize the acidity. The most common method used to passively generate alkalinity is the construction of a wetland that

contains an organic substrate in which alkalinity-generating microbial processes occur. If the substrate contains limestone, as spent mushroom compost does, then alkalinity will be generated by both calcite dissolution and bacterial sulfate reduction reactions. These alkalinity generating processes are slow relative to processes that remove Fe. Thus, the performance of the constructed wetlands that receive acidic water is usually limited by the rate at which alkalinity is generated within the substrate. While wetlands can significantly improve water quality, and have proven to be effective at moderately acidic sites, no wetland systems that consistently and completely transform highly acidic water to compliance quality are known. Inconsistent or partial treatment indicates undersizing. The authors believe this is because of a lack of awareness of how much larger wetlands constructed to treat acidic water must be than ones constructed to treat alkaline water. The Fe and acidity removal rates measured in this study indicate that the treatment of 5,000 $g \cdot d^{-1}$ of Fe in alkaline water requires ~250 m^2 of aerobic wetland. The treatment of the same Fe load in acidic water (where treatment requires both precipitation of the Fe and neutralization of the associated acidity) requires ~1,300 m^2 of compost wetland. Thus wetlands constructed to treat acidic water need to be six times larger than ones constructed to treat similarly contaminated alkaline water.

The recent development of limestone pretreatment systems, e.g., the anoxic limestone drain, is a significant advancement in passive treatment technology. When successful, ALD's can lower acidities or actually transform acidic water into alkaline water, and markedly decrease the sizing demands of the wetlands constructed to precipitate the metal contaminants. Because limestone is inexpensive, the cost of an ALD-aerobic wetland passive treatment system is typically much less than the compost wetland alternative. Thus, when the influent water is appropriate, ALD's should be the preferred method for generating alkalinity in passive treatment systems.

Anoxic limestone drains have also been used to increase the performance of existing constructed wetlands. At many poorly performing wetlands that receive acidic water, the wetland was built too small to treat an acidic, metal-contaminated influent, but is large enough for an alkaline, metal-contaminated influent. One of the study sites, the Morrison wetland, was undersized for the highly acidic water that it received. As a result, the wetland effluent required supplemental treatment with chemicals. Since construction of an ALD, and its addition of 275 $mg \cdot L^{-1}$ of bicarbonate alkalinity to the water, the discharge of the wetland has been alkaline, low in dissolved metals, and does not require any supplemental chemical treatment. Similar enhancements in wetland performance through the addition of ALD's have been reported elsewhere in Appalachia (*15, 18*).

KINETICS OF CONTAMINANT REMOVAL PROCESSES

This report presents an intensive analysis of contaminant removal kinetics in passive treatment systems. The rates presented are generally in agreement with those reported by other investigators. For example, the average Mn-removal rate measured in this study for alkaline, Fe-free waters, 0.5 $g \cdot m^{-2} \cdot d^{-1}$, is consistent with rates reported by the TVA for aerobic wetlands in southern Appalachia (*18*) and by the Pennsylvania Department of Environmental Resources (DER) for constructed wetlands in Pennsylvania (*60*). The average Fe-removal rate reported in this study for alkaline waters, 20 $g \cdot m^{-2} \cdot d^{-1}$, is only slightly greater than has been reported in other studies. The rates of Fe removal for aerobic wetlands in southern Appalachia ranged from 6 to 20 $g \cdot m^{-2} \cdot d^{-1}$ (*18*). Some of the lower rates reported by TVA investigators, however, are from wetland systems that discharge water with <1 $mg \cdot L^{-1}$ Fe and thus are loading limited with respect to Fe. Such sites were intentionally avoided in this study. Stark (*17*), in their studies of a constructed wetland in Ohio, reported Fe removal rates over a range of loading conditions. When the wetland system discharged >15 $mg \cdot L^{-1}$ Fe, and thus was overloaded with Fe, the removal rate averaged 21 $g \cdot m^{-2} \cdot d^{-1}$. When the wetland effluent contained <15 $mg \cdot L^{-1}$ Fe, the removal rate averaged only 11 $g \cdot m^{-2} \cdot d^{-1}$.

LONG-TERM PERFORMANCE

Passive treatment systems cannot be expected to perform indefinitely. In the long term, wetland systems will fill up with metal precipitates or the conditions that facilitate contaminant removal may be compromised. None of the treatment systems considered in this study demonstrated any downward trends in contaminant removal performance. Therefore, estimates of the long-term performance of passive systems must be made by extrapolating available data. Like the design and sizing of passive treatment systems, estimates of long-term performance vary with the chemistry of the mine water. Systems receiving alkaline water precipitate Fe and Mn contaminants by oxidative processes. The rapid removal of Fe that occurs in alkaline treatment systems means that such systems will inevitably fill up. Stark (*61*) reports that the Fe sludge in a constructed wetland in Ohio is increasing by 3 to 4 cm per year. Similar measurements at Pennsylvania wetlands indicate an increase in sludge depth of 2 to 3 cm per year (*62*). These measurements suggest that dikes that provide 1 m of freeboard should provide sufficient volume for 25 to 50 years of performance.

At some surface mines, water quality tends to improve within a decade after regrading and reclamation are

completed (*63-64*). At these surface minesites, 25 to 50 years of passive treatment may be adequate to mitigate the contaminant problem. At surface mine sites where contaminant production is continual, or at systems constructed to treat drainage from underground mines or coal refuse disposal areas, the system can either be built with greater freeboard or rebuilt when it eventually fills up. Site conditions will determine whether it is more economical to simply bury the wetland system in place and construct a new one, or to excavate and haul away the accumulated solids for proper disposal. Disposal of these excavated sludges is not difficult or unduly expensive because the material is not considered a hazardous waste.

Wetlands that receive acidic water, and function through the alkalinity-generating processes associated with an organic substrate, may decline in performance as the components of the organic substrate that generate alkalinity are exhausted. The compost wetlands described in this report neutralize acidity through the dissolution of limestone and the bacterial reduction of sulfate. Limestone dissolution is limited by the amount of limestone present in the substrate. The limestone content of spent mushroom compost is ~30 $kg \cdot m^{-3}$ (*65*). If a wetland containing a 40 cm depth of compost generates $CaCO_3$-derived alkalinity at a mean rate of 3 $g \cdot m^{-2} \cdot d^{-1}$ (the average rate measured in this study), then the limestone content of the compost will be exhausted in 11 years. The same volume of compost contains ~40 kg of organic carbon. If bacterial sulfate reduction mineralizes 100% of this carbon to bicarbonate at a rate of 5 $g \cdot m^{-2} \cdot d^{-1}$, then the carbon will be exhausted in 91 years. This estimate is increased by the carbon input of the net primary production of the wetland system, but decreased by the fact that some of the carbon is mineralized by reactions other than sulfate reduction. Studies of a salt marsh on Cape Cod, MA, indicated that 75% of the carbon was eventually mineralized by sulfate reduction processes (*66*). Another significant factor that decreases the available carbon is that a portion of the carbon pool is recalcitrant.

A realistic scenario for the long-term performance of a compost wetland is that sulfate reduction is linked, in a dependent manner, to limestone dissolution. Sulfate-reducing bacteria are inactive at pH less than 5 (*37*). Their activity in a wetland receiving lower pH water may depend, in part, on the presence of pH-buffering supplied by limestone dissolution. Thus, limestone dissolution may create alkaline zones in which sulfate reduction can proceed and produce further alkalinity. If this scenario is accurate, then the long-term performance of a compost wetland may be limited by the amount of limestone in the substrate, or according to the above calculations, about 11 years of performance. Under these conditions it would be advisable to increase the chemical buffering capability of the wetland substrate by adding additional limestone during wetland construction. In fact, this procedure is commonly practiced at many constructed compost wetland sites.

The performance of anoxic limestone drains has many aspects that make long-term expectations uncertain. Anoxic limestone drains function through the dissolution, and thus removal, of limestone. Eventually, this chemical reaction will exhaust the limestone. Long-term scenarios about ALD performance fail to consider the hydrologic implications of the gradual structural failure of the systems. In large ALD's, most of the limestone dissolution occurs in the upgradient portion of the limestone bed. It is unknown whether this preferential dissolution will produce partial failure of the integrity of the system or whether the permeability will be adversely affected. Another aspect that affects long-term ALD performance is the fact that ALD's retain ferric iron and aluminum (*34-35*). This retention has raised concerns about the armoring of limestone or the plugging of flow paths long before the limestone is exhausted by dissolution reactions (*34*). No methods are currently available to predict exactly how the retention of these metals affects the performance of ALD's.

CONTINUALLY EVOLVING PASSIVE TECHNOLOGIES

This document reports the current state of passive mine water treatment technologies. The design and sizing recommendations presented herein represent current methodologies that will subsequently be replaced with more efficient techniques. For example, important experiments are underway in Pennsylvania, Virginia, and West Virginia testing "hybrid" ALD-compost wetland systems. In these experimental systems, organic substrates are used to reduce ferric iron to ferrous iron and strip dissolved oxygen from the water so that the mine water is suitable for flow through an anoxic limestone drain. If these systems prove successful, it may be possible to treat highly acidic water by cycling it between anoxic alkalinity-generating environments and aerobic, metal-removal environments. Experimental systems using this design have recently been constructed in western Pennsylvania (*67*).

While the specific tools of passive treatment are likely to evolve in the coming years, the fundamental mechanisms of passive treatment that have been identified in this report will probably not change markedly. Research has shown that the treatment of contaminated coal mine drainage by constructed wetlands can be explained by well-known chemical and biological processes. Passive treatment, like active treatment with chemicals, requires that the metal contaminants be precipitated and that the acidity associated with these ions be neutralized. By recognizing that these treatment goals need not be accomplished

simultaneously, one can focus on optimization of the individual objectives. As a result, the performance and cost effectiveness of passive treatment systems is rapidly improving. Today, most mine operators who install properly designed passive treatment systems rapidly recoup the cost of their investment through decreased water treatment costs. There is no reason to doubt that this technology will continue to improve and that, over time, passive treatment will be used in applications that are not possible today.

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