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

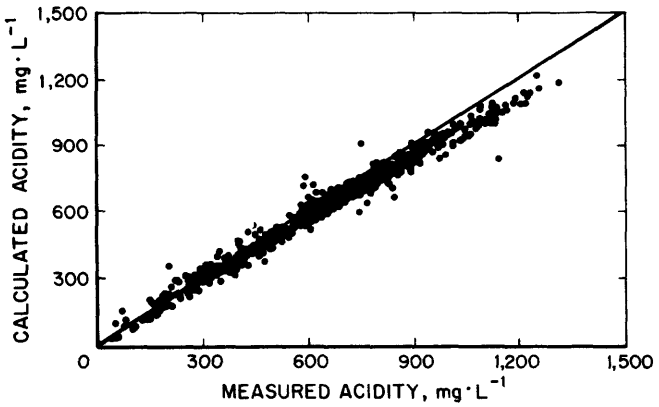

Figure 1.—Comparison of calculated and measured acidities for water samples collected at Friendship Hill wetland.

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, $mg \cdot L^{-1}$	Al, $mg \cdot L^{-1}$	Fe^{2+}, $mg \cdot L^{-1}$	Fe^{3+}, $mg \cdot L^{-1}$	Mn, $mg \cdot L^{-1}$	SO_4, $mg \cdot L^{-1}$	Net alkalinity,[1] $mg \cdot L^{-1}$
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 $mg \cdot L^{-1}$ alkalinity for each 1.0 $mg \cdot L^{-1}$ 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

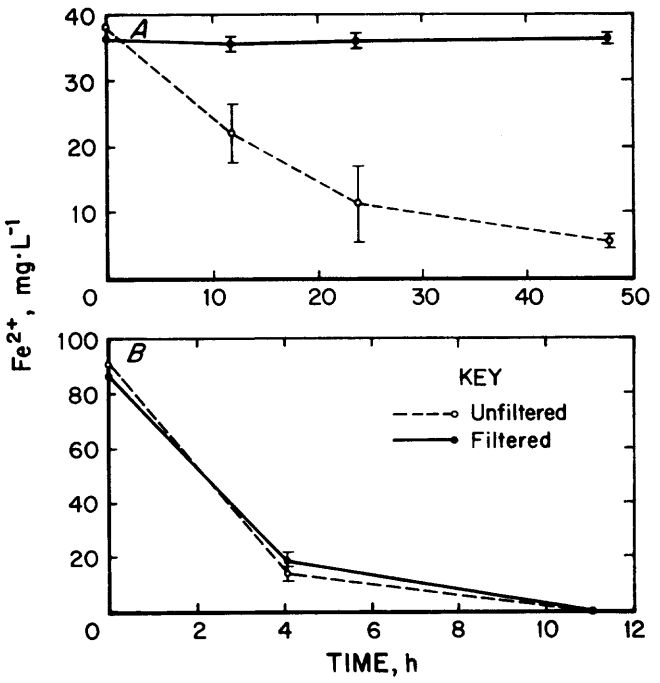

Figure 2.—Removal of Fe^{2+} from acidic and alkaline mine waters in laboratory experiment. Raw mine drainage was collected from *A*, acidic Latrobe site; *B*, alkaline Cedar Grove site. Splits of each sample were filter-sterilized (0.22-μm filter). The Latrobe samples were shaken throughout experiment;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

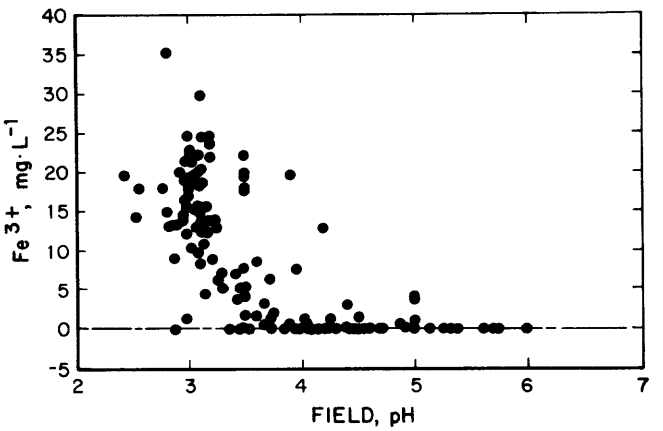

Figure 3.— Concentrations of Fe^{3+} and field pH for water samples collected from Emlenton wetland.

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 aerobic 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•L^{-1}, while Mn decreased from 42 to 11 mg•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

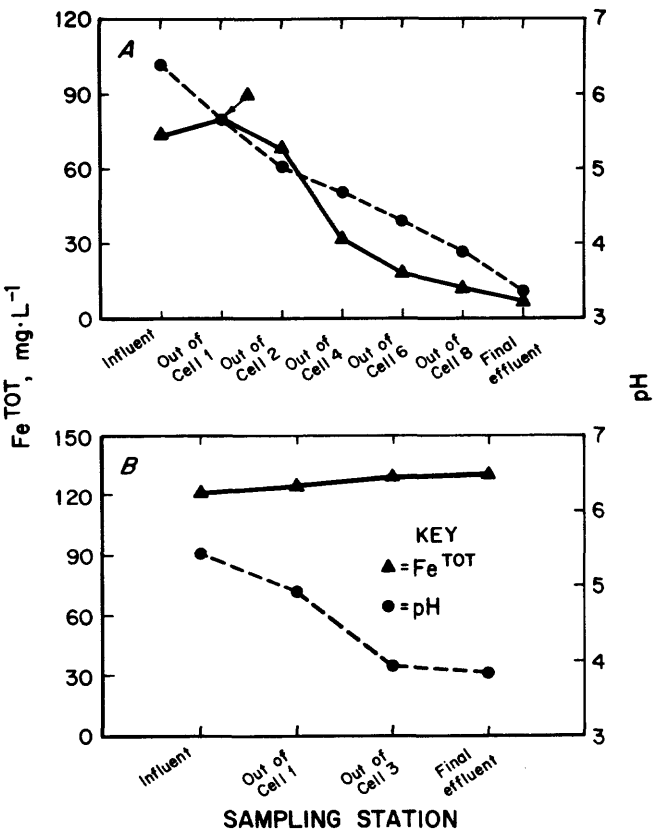

Figure 4.—Concentrations of Fe^{tot} and field pH at two constructed wetlands. *A*, Emlenton wetland; *B*, Cedar Grove wetland.

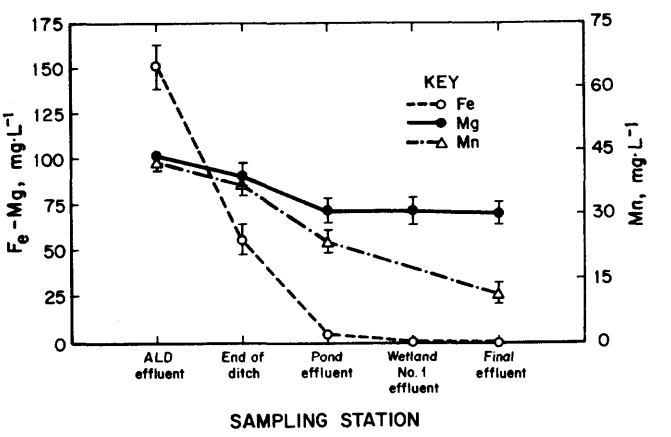

Figure 5.—Mean concentrations of Fe, Mn, and Mg at the Morrison Wetland. Mine water flows linearly from station 1 to station 5. Verticle bars are one standard error of the mean.

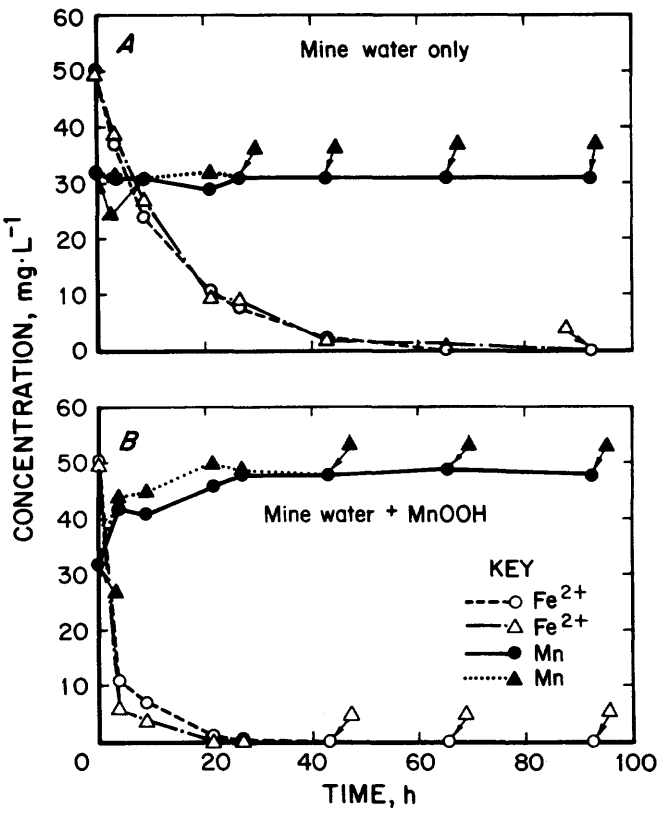

Figure 6.—Changes in concentrations of Fe^{2+} and Mn^{2+}. *A*, absence; *B*, presence of MnOOH. Mine water was collected from influent pipe of Blair wetland. MnOOH was collected from inside of final effluent pipe.

collected from a wetland that removed Fe and Mn in a sequential manner. The wetland influent was alkaline (pH 6.2, 162 $mg \cdot L^{-1}$ alkalinity) and contaminated with 50 $mg \cdot L^{-1}$ Fe and 32 $mg \cdot L^{-1}$ 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 $mg \cdot L^{-1}$. In the control flasks, concentrations of Fe decreased to <3 $mg \cdot L^{-1}$ within 43 h. In flasks that received MnO_2, concentrations of Fe decreased to <3 $mg \cdot L^{-1}$ 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 $mg \cdot L^{-1}$ 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.

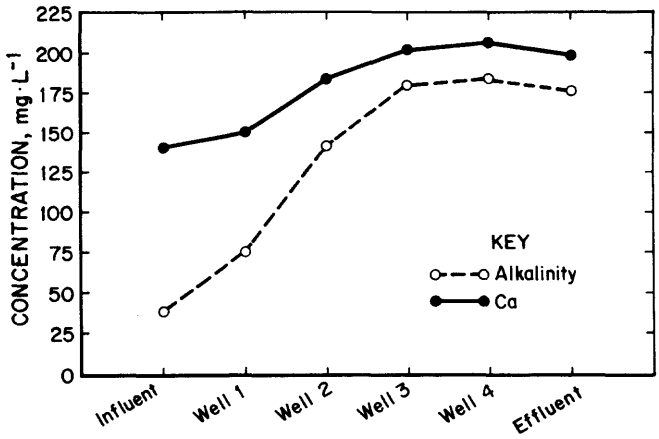

Figure 7.—Concentrations of Ca, and alkalinity for water as it flows through the Howe Bridge ALD. Water flows linearly from influent to effluent.

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 ($\ll$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
$H_2S + 2HCO_3^- + ½O_2 \rightarrow S^0 + H_2O + 2HCO_3^-$	0	+100
$H_2S + 2HCO_3^- + FeS + ½O_2 \rightarrow FeS_2 + H_2O + 2HCO_3^-$	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).

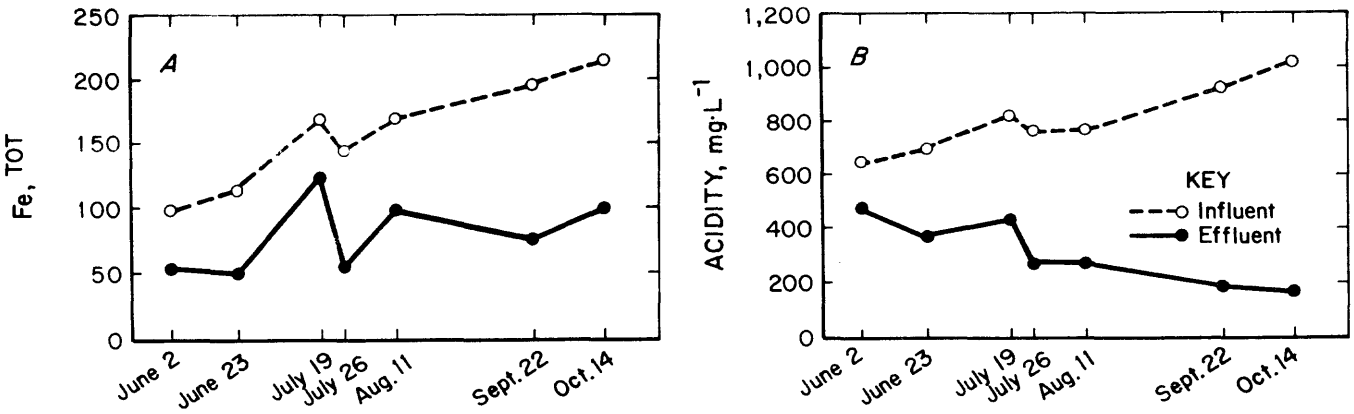

Figure 8.—Influent and effluent concentrations at the Latrobe wetland during the summer of 1988. *A*, Fe; *B*, acidity.

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