Selection of Reactive Mixtures for Use in Permeable Reactive Walls for Treatment of Mine Drainage

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Porous, permeable, geochemically reactive walls, installed in situ in the path of migrating groundwater, present a promising passive treatment alternative for remediating metal-contaminated groundwater derived from oxidized mine wastes. Contaminants are removed from the groundwater as a result of bacterial sulfate reduction and the subsequent precipitation of sparingly soluble sulfide solids. The permeability and reactivity of eight organic-carbon reactive mixtures were assessed. The permeability ranged between $<10^{-4}$ and 10^{-2} cm/s. Batch tests conducted using simulated mine drainage indicated that, within 40−70 days, SO_4 concentrations decreased from initial concentrations of 1200−4800 mg/L to final concentrations of <10 mg/L in four mixtures. Iron concentrations decreased from initial concentrations of between 105 and 1400 mg/L to concentrations between 0.1 and 50 mg/L within 0.1−65 days. Concentrations of 480 mg/L Ni and 135 mg/L Cd decreased to below 0.05 mg/L within 10 days. pH and alkalinity values increased from initial pH values of <6 to values of 6.5−7 and alkalinity values (as $CaCO_3$) of <15 mg/L to >1000 mg/L. Geochemical model calculations suggest precipitation of Fe and Zn sulfide phases and the Mn carbonate phase rhodochrosite. The reactivity of the mixtures varied with those containing several organic sources being most reactive. Results obtained from these studies indicate that levels of reactivity and permeability suitable for remediating tailings-impacted groundwater can be attained.
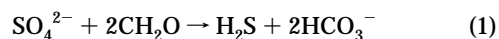
Introduction

The mining and milling of sulfidic ore deposits generates large quantities of sulfide-bearing waste rock and finely crushed mill tailings. The mine tailings are mixed with mill process water and deposited as a slurry within impoundments. Upon decommissioning, an unsaturated zone develops as the original mill process water drains naturally through the underlying geologic material. Atmospheric oxygen diffuses into the unsaturated zone and is consumed through oxidation reactions (*1, 2*).

Oxidation of pyrite (FeS_2), pyrrhotite [$Fe_{(1-x)}S$], and other metal-sulfide minerals within the unsaturated zone of mine-tailings impoundments results in low-quality pore water

characterized by low pH and elevated concentrations of SO_4, Fe(II), and other dissolved metals (*1, 2*). This water may be transported downward through the tailings where it undergoes a series of acid neutralization and secondary mineral-precipitation reactions (*1, 3, 4*). The resulting water, characterized by neutral pH and elevated concentrations of dissolved SO_4, Fe(II), and low to moderate concentrations of metals, can migrate into the groundwater-flow system and ultimately discharge into oxygenated surface-water bodies releasing dissolved metals and acidity.

Present techniques for controlling or treating mine drainage include minimizing sulfide oxidation, collecting and treating the acidic water, and controlling the migration of tailings pore water (*5*). An alternative approach to treating mine drainage is through the use of enhanced bacterially mediated sulfate reduction. Tuttle et al. (*6*) observed sulfate reduction, accompanied with increases in pH, in mine discharge water after passage through a wood dam. More recent studies have focused on above ground-surface treatment of oxidized mine-drainage water characterized by low pH and elevated concentrations of dissolved SO_4, Fe(III), and other metals (*7, 8*). Further development of this approach has focused on remediating mine drainage through the use of permeable, geochemically reactive walls which are installed below the ground surface in the path of migrating tailings-impacted water (Figure 1) (*9*). These geochemically engineered walls are designed to enhance biologically mediated sulfate reduction through the addition of reactive solids (*10, 11*). Tailings-impacted groundwater is treated before being discharged into an oxygenated surface-water body, thereby preventing the oxidation of Fe(II), the precipitation of Fe(III) oxyhydroxides, and the generation of acidic drainage.

Under favorable conditions sulfate-reducing bacteria (SRB) convert sulfate to sulfide by catalyzing the oxidation of organic carbon coupled with the reduction of sulfate (*12*):

$$SO_4{}^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3{}^- \tag{1}$$

where CH_2O represents a simple organic carbon. Sulfate-reduction reactions consume SO_4, produce H_2S, and result in an increase in alkalinity and pH (*6*). Increases in dissolved H_2S concentrations enhance the precipitation of metals as metal sulfides:

$$Me^{2+} + S^{2-} \rightarrow MeS \tag{2}$$

where Me^{2+} denotes a divalent metal such as Cd, Fe, Ni, Cu, Co, and Zn.

This paper describes experiments, conducted to determine favorable mixtures for use in in situ permeable reactive walls. Batch experiments were designed to be representative of the field conditions.

Methodology

Batch Reaction Flasks. Glass reaction flasks, 500 and 1000 mL, containing two sampling ports, were used for the experiments. The sampling ports were fitted with Teflon-lined septa so that substances could be removed or added by piercing these septa with a syringe.

The chemical composition of the simulated mine water was based upon a groundwater plume downgradient from the Nickel Rim mine site near Sudbury, ON (*13*). The simulated mine drainage water was prepared by adding 3620 mg/L SO_4, 1080 mg/L Fe, 0.81 mg/L Zn, and 1.15 mg/L Ni to $CaCO_3$ saturated deionized water. The pH of the solution was 5.5−6.5, the alkalinity was <30 mg/L as $CaCO_3$. The
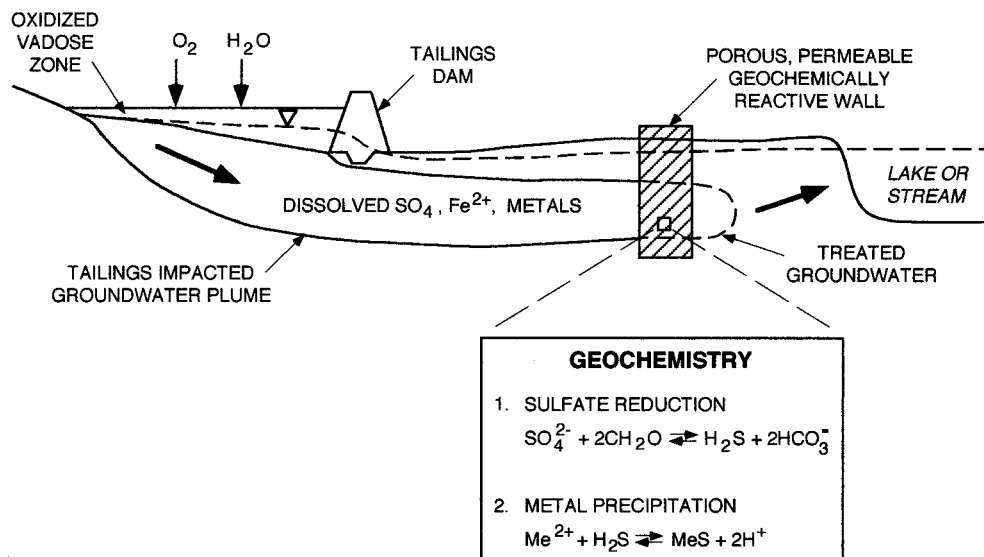
FIGURE 1. Schematic of a permeable reactive wall at a mine-tailings site.

TABLE 1. Organic Substrates Used in Batch Reactive Mixtures as Dry Weight Percent (wt %)

batch mixture	sewage sludge	leaf mulch	wood chips	sheep manure	sawdust	cellulose
1	100					
2					100	
3		100				
4		10		65	25	
5	20	10	25	20	25	
6		60			40	
7	15	60	15		10	
8						100

TABLE 2. Composition of Batch Reactive Mixtures with Solids Given as Dry Weight Percent (wt %) and Simulated Mine-Drainage Water as a Volume (mL)

batch mixture	organic carbon (wt %)	creek sediment (wt %)	silica sand (wt %)	agricultural limestone (wt %)	total mass solids (g)	vol simulated mine drainage (mL)
1	73	14	11	2	219	376
2	56	24	18	2	137	413
3	27	38	32	3	77	466
4	57	25	15	3	166	891
5	46	34	18	2	81	470
6	31	43	19	7	128	897
7	48	35	13	4	114	857
8	19	60	17	4	117	959

solution also contained Mn, Na, Ca, K, and Mg which were added as sulfate salts.

Eight reactive mixtures were prepared. Each mixture consisted of four main components: an organic source or sources (Table 1), a bacterial source, a neutralizing agent, and a nonreactive porous medium (Table 2). Six carbon sources were chosen: (1) composted leaf mulch, primarily mixed deciduous leaves derived from a municipal recycling program, (2) composted municipal sewage sludge, (3) maple sawdust, (4) mixed hardwood and softwood chips, (5) composted sheep manure, and (6) delignified waste cellulose. The bacterial source was collected from the anaerobic zone of a local creek. Less than 15% creek sediment by volume, 60 wt %, was added to the reactive mixtures. Agricultural limestone was added to each mixture at approximately 1−2%

of the total volume, 2−7 wt %. Silica sand was added to the mixtures to increase the permeability, between 5 and 10% of the total volume, 11−32 wt %.

After the mixtures were added, the flasks were completely filled with deoxygenated simulated mine water, solid $FeSO_4 \cdot 7H_2O$ and $CaSO_4$ were added, then the flasks sealed. The amount of simulated mine water added to each flask was dependent upon the volume of the reactive mixture and the size of the flask (Table 2). A second addition of simulated mine water was added to several mixtures to assess the reactivity over time. The simulated mine water added to one of the batch mixtures (mixture 7) was also spiked with high concentrations of Ni, Cd, Zn, and Pb. Reaction flasks were vented to allow excess gas to escape.

Sample Collection. The batch experiments were sampled as a function of time in a manner designed to minimize O_2 exposure. Measurements of pH (ORION ROSS 81-00-07 Combination electrode), E_h (ORION 96-78-00 Combination electrode), and alkalinity were determined immediately after sample collection. Alkalinity was determined on a filtered sample using standardized H_2SO_4. Samples were filtered through 0.45 μm cellulose acetate filters. H_2S concentrations were determined using the methylene blue spectrophotometric method (14). o-Phosphate analyses were conducted using the ascorbic acid spectrophotometric method (15). Concentrations of cations (Ba, Ca, Cd, Fe, K, Mg, Mn, Na, Ni, Pb, and Zn) were determined on acidified samples using inductively coupled plasma atomic emission spectroscopy (ICP-AES), SO_4 analyses were conducted using either ion chromatography (IC) or the automated methylthymol blue spectrophotometric method (15), NH_4 concentrations were determined using IC, and DIC/DOC were determined using infrared detection (IR). Iron concentrations were also determined using the Ferrozine method of Gibbs (16). Representative samples of each of the six solid organic sources used were analyzed for total combustible carbon using LECO SC444 and IR, and total N and P were determined using a modified Kjeldahl method.

The permeability of the most reactive organic mixtures was measured using falling-head permeameter test cells using the technique described by Sudicky (17). Samples were dried and saturated with CO_2 prior to measurement.

Geochemical Modeling. The geochemical computer code MINTEQA2 (18) was used to calculate the saturation indices (SI) of various mineral phases. The original database was modified to make it consistent with the WATEQ4F database (19), and additional solubility data were added for siderite
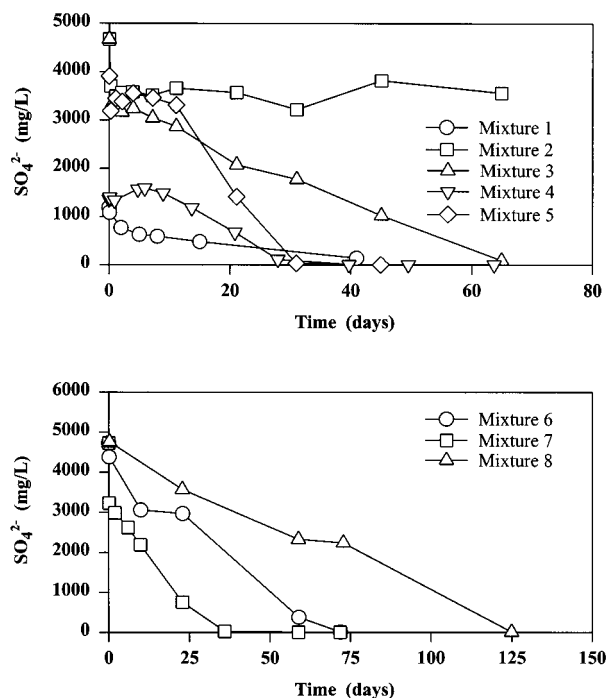
FIGURE 2. Sulfate removal versus time for batch mixtures 1–8.

based upon values reported by Nordstrom et al. (*20*) and Ptacek (*21*).

Results and Discussion

Sulfate Removal and Changes in Concentrations of Dissolved Constituents. Sulfate-reducing conditions were developed within 3 weeks in all mixtures except the reactive mixtures containing only sheep manure (mixture 2), and only cellulose (mixture 8). Acclimation was indicated by SO_4 removal, lowered E_h values, and generation of alkalinity and H_2S. The mixture containing sewage sludge (mixture 1) was the most rapid to acclimate.

Sulfate removal was observed in all of the batch experiments (Figure 2). In the mixture containing a combination of organic sources, sheep manure, sawdust, and leaf mulch (mixture 4), the SO_4 concentration decreased from 1200 mg/L to <10 mg/L in 26 days; for the batch mixture containing everything except cellulose (mixture 5), the SO_4 concentration decreased from 3300 mg/L to <35 mg/L in 20 days; and the mixture containing leaf mulch, wood chips, sewage sludge and sawdust (mixture 7) decreased from 4800 mg/L to <25 mg/L in 35 days. After 65 days, the SO_4 concentration in the mixture containing only sheep manure as an organic carbon source (mixture 2) decreased from 4700 mg/L to 3600 mg/L. Due to this low reactivity, mixture 2 was eliminated from further testing.

Corresponding to decreased SO_4 concentrations were increased concentrations of H_2S. Initially, H_2S concentrations were below detection and concentrations increased to between 35 and 75 mg/L in the batch mixtures containing leaf mulch and sawdust (mixture 6), leaf mulch, wood chips, sewage sludge and sawdust (mixture 7), and cellulose (mixture 8). These results suggest that SO_4 removal was the result of sulfate-reduction reactions. Alkalinity increases were observed for each of the measured reactive mixtures with typical increases from <0.1 mg/L in the simulated mine drainage to between 2000 and 4000 mg/L as $CaCO_3$ in the sample water (Figures 3 and 4).

Sulfate-Reduction Rates. During the batch studies, the solution-to-solid ratio decreased as the simulated mine water was removed for sample collection. The changes in water volume were not recorded. As a result, precise estimates of

the sulfate reduction rates cannot be calculated on the basis of the mass of sulfate. The sampling protocol used prevents the calculation of sulfate reduction rates using the technique described by Hedin et al. (*22*) and Wildeman and Updegraff (*23*), which relies on an accounting of the sulfate mass. Under closed, anoxic systems, however, rates of bacterially mediated sulfate reduction can be approximated by sulfate-removal rates (*24*). These rates are considered approximate because other processes, such as differing solid-solution ratios, adsorption of SO_4 to ferric oxyhydroxides, acclimation periods, and concentrations of SO_4 and H_2S, also affect the calculated sulfate-reduction rates (*25, 26*). At early times when the pH is less than 7 and the system is slightly oxidizing (i.e., >0 mV), loss of SO_4 due to adsorption onto ferric oxyhydroxides may have occurred. At later times, minimal adsorption of SO_4 is expected because of the loss of ferric oxyhydroxides due to reductive dissolution reactions.

Sulfate-reduction rates were compared using linear least-squares regression analysis, disregarding early-time data which may have been affected by acclimation periods and adsorption and late-time data which may have been SO_4 limited (Table 3). Sulfate made available through dissolution of gypsum added to the creek sediment was not considered in the calculated sulfate-reduction rate.

After the acclimation period, sulfate-reduction rates were generally higher in the reactive mixtures which contained a variety of organic sources. Reactive mixture 5, containing five different organic sources, had the highest sulfate-reduction rate (-4.23 mg L^{-1} day^{-1} g^{-1} of organic matter), and batch mixture 1, containing only sewage sludge, had the lowest measured rate of SO_4 removal (-0.14 mg L^{-1} day^{-1} g^{-1}). The higher sulfate-removal rates may have been influenced by the C, N, and P contents. In addition to C, sulfate-reducing bacteria require N and P for metabolic function (*25, 26*). Total C, N, and P analyses were conducted on the organic sources (Table 4) and calculated for each mixture.

The materials used in mixtures 1 and 2, composted sewage sludge and composted sheep manure, respectively, had the lowest C content (9–11%) compared to the other materials (35–47%). Mixtures 1 and 2 were the least reactive. Mixtures 3 (leaf mulch), 5 (without cellulose), 6 (leaf mulch and sawdust), and 7 (leaf mulch, wood chips, sewage sludge, and sawdust) showed the highest rates of SO_4 reduction (-1.52 to -4.23 mg L^{-1} day^{-1} g^{-1}); these mixtures also had the highest C contents. Mixture 8 (cellulose) had a high C content but a slightly lower calculated rate of sulfate reduction (-1.18 mg L^{-1} day^{-1} g^{-1}). The total N content of the cellulose was low (0.01 mg/L) and P was below detection, suggesting that rates of sulfate reduction may also be dependent upon N and P content.

Aqueous concentrations of NH_4, o-PO_4, and DOC were determined on several water samples from mixtures 4 and 5 (Table 5). Also given in Table 5 are the concentrations of SO_4 for comparison. Mixture 4, which contained 65 wt % composted sheep manure, plus sawdust and leaf mulch, had one of the lowest sulfate-reduction rates.

Results showed that NH_4 concentrations decreased over time. Ammonia concentrations in mixture 4 decreased from 22 mg/L to <0.3 mg/L while SO_4, o-PO_4, and DOC concentrations remained high; in comparison, concentrations of NH_4 in mixture 5 (without cellulose) were not completely depleted until the concentration of SO_4 had decreased from 4000 mg/L to 30 mg/L. The calculated sulfate-reduction rates were higher in batch mixture 5 than in mixture 4 (-4.23 mg L^{-1} day^{-1} g^{-1} versus -0.76 mg L^{-1} day^{-1} g^{-1}), suggesting that N may have limited the rate of sulfate reduction in mixture 4. Mixture 4 had a higher solid N content than mixture 5, which suggests that rates of organic C degradation and lability of C, N, and P did not directly correspond to the total solid-phase C, N, and P content.
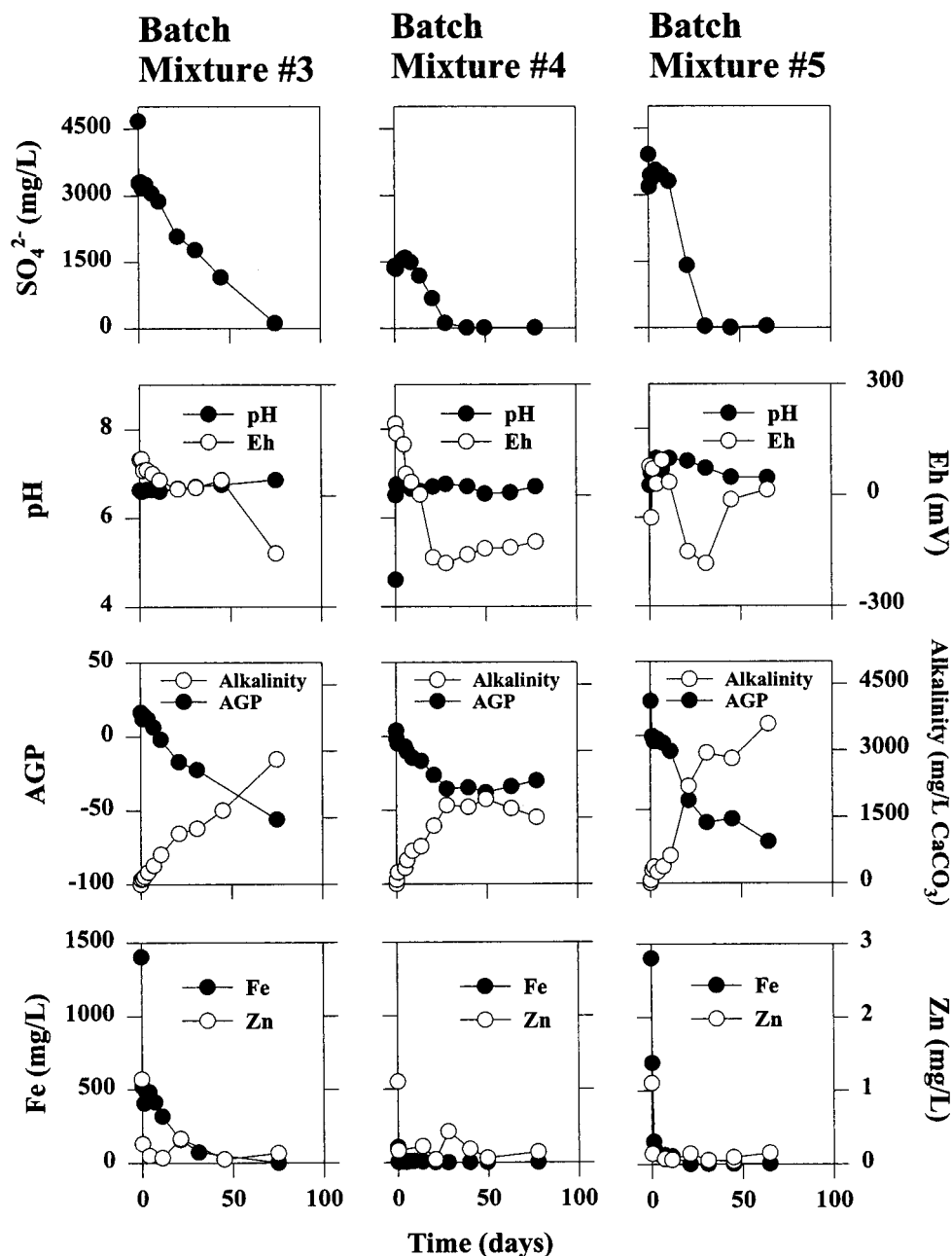
FIGURE 3. Concentrations of dissolved SO$_4$, Fe, and Zn, pH, Eh alkalinity, and calculated acid-generating potential (AGP) for batch mixtures 3—5 as a function of time.

The experiments in this study were conducted at room temperature. Sulfate-reduction rates determined at this temperature may not be directly transferable to lower-temperature field conditions. It is anticipated, however, that the relative rates of reaction associated with an individual substrate would be similar at lower temperatures. Sulfate-reducing bacteria can tolerate temperatures from below −5 °C to 75 °C and are adaptable to new temperature conditions (27). Studies by Herlihy et al. (28) on the rate of sulfate reduction in natural environments indicate that temperature does not substantially affect the sulfate-removal rate.

Changes in pH and Metal Concentrations over Time. If sufficient reduction of SO$_4$ occurs, the pH will be buffered by carbonate equilibrium reactions typically in the range 6—7 (29). An increase in pH from below 5 to between 6 and 7 was observed in all of the batch mixtures except the mixture containing only sewage sludge as an organic carbon source (mixture 1), which increased to pH 12 a few hours after adding the simulated mine water (Figures 3 and 4, mixtures 1 and

2 not shown). The large increase in pH made the use of this organic source impractical; therefore, mixture 1 was eliminated from further testing.

Concentrations of dissolved Fe and other metals were assessed in the remaining six reactive mixtures (mixtures 3—8). Metal concentrations decreased rapidly and remained low. Concentrations of Fe were depleted within hours to days (Figures 3 and 5).

Tailings-derived water with high concentrations of Fe(II) has the potential to generate acidity upon discharge into an oxygenated surface-water body through the reactions

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

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \qquad (4)$$
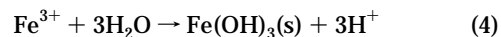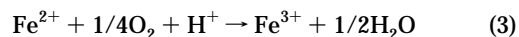
In the presence of O$_2$, Fe(II) rapidly oxidizes to Fe(III) (eq 3), Fe(III) in turn hydrolyzes to form an insoluble ferric oxy-
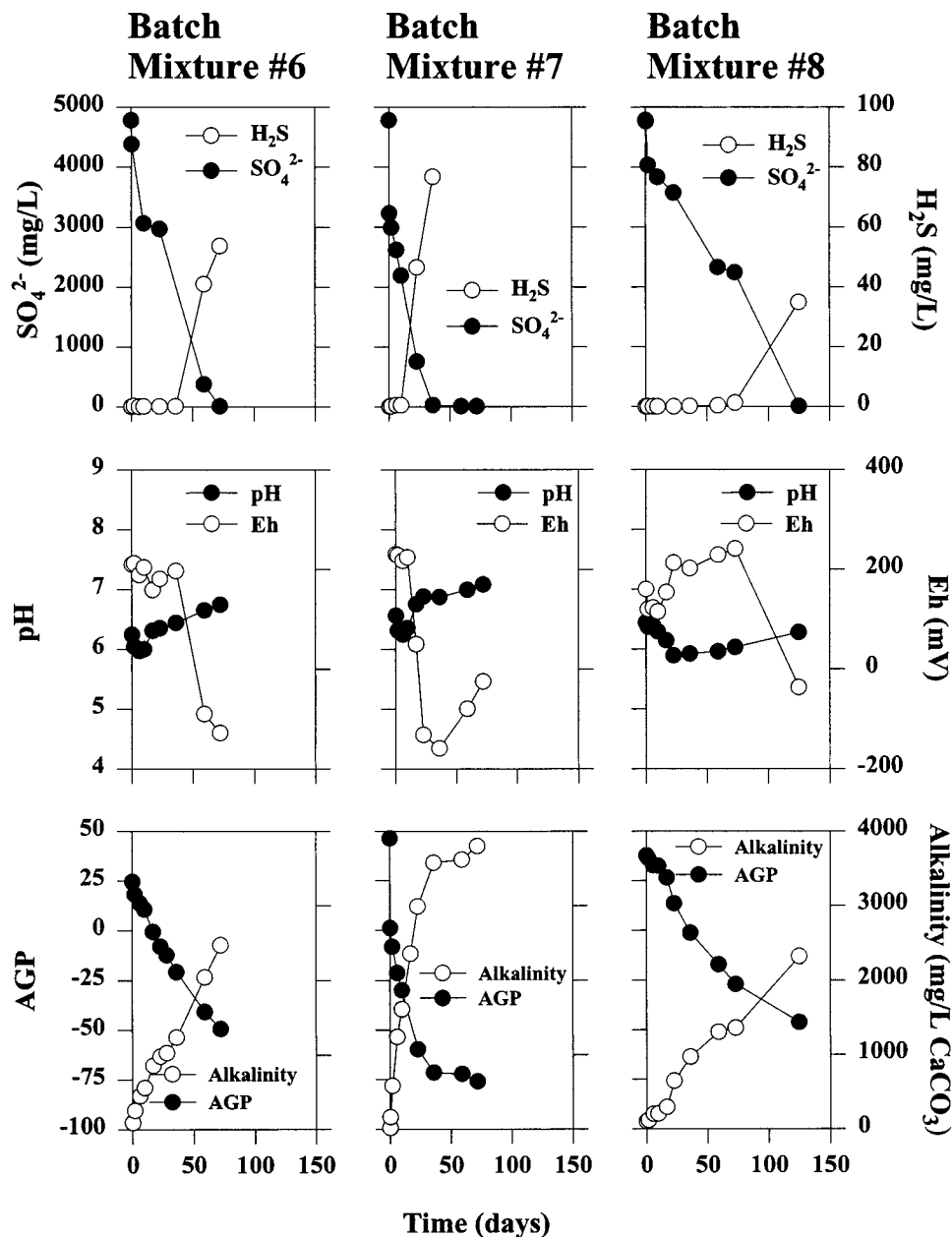
FIGURE 4. Concentrations of dissolved SO_4 and H_2S, pH, Eh, alkalinity, and calculated acid-generating potential (AGP) for batch mixtures 6−8 as a function of time.

hydroxide or hydroxide solid, represented here as ferric hydroxide. Ferric hydroxide precipitation releases H^+ (eq 4). The acid-generating potentials (AGP) of batch mixtures 3−8 were calculated by determining the acid-producing potential (APP) through the oxidation of Fe(II) to $Fe(OH)_3$ (eq 3 and 4), which releases 2 mol of H^+ for every mole of Fe(II) oxidized and subtracting from this the acid-consuming potential (ACP) or alkalinity (as mg/L $CaCO_3$). One mole of $CaCO_3$ can consume 2 mol of H^+ as shown by the following reaction:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + H_2CO_3 \qquad (5)$$
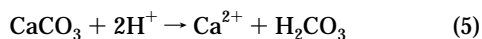
A negative AGP value indicates a capacity to neutralize acid while a positive value indicates a potential to generate acidity upon exposure to an oxidizing environment. Initially, the AGP ranged from 25−50 (as milliequivalent H^+/L) and over time as Fe was removed and alkalinity increased (Figures 3

and 4) the AGP decreased to between −18 and −75 (as milliequivalent H^+/L), thus resulting in a net acid-consuming potential (Figures 3 and 4).

Results from three mixtures (mixtures 6−8) show dissolved H_2S concentrations increased from below detection to concentrations between 35 and 75 mg/L after metal concentrations were depleted after 16−72 days (Figure 4). These results suggest that early H_2S concentrations (i.e., the first 16−72 days) were controlled by metal-sulfide precipitation reactions with H_2S concentrations increasing only after metal concentrations were depleted.

Analyses of the major ions Ca, Mg, Na, and K for batch mixtures 6, 7, and 8 show relatively constant concentrations of Mg, Na, and K after the simulated mine water was added to the reaction flasks (Figure 5). Concentrations of Ca initially increased over time in all three of the batch mixtures from 400 mg/L in the input solution to between 800 and 1200 mg/L in the sample water after 1−35 days. Calcium
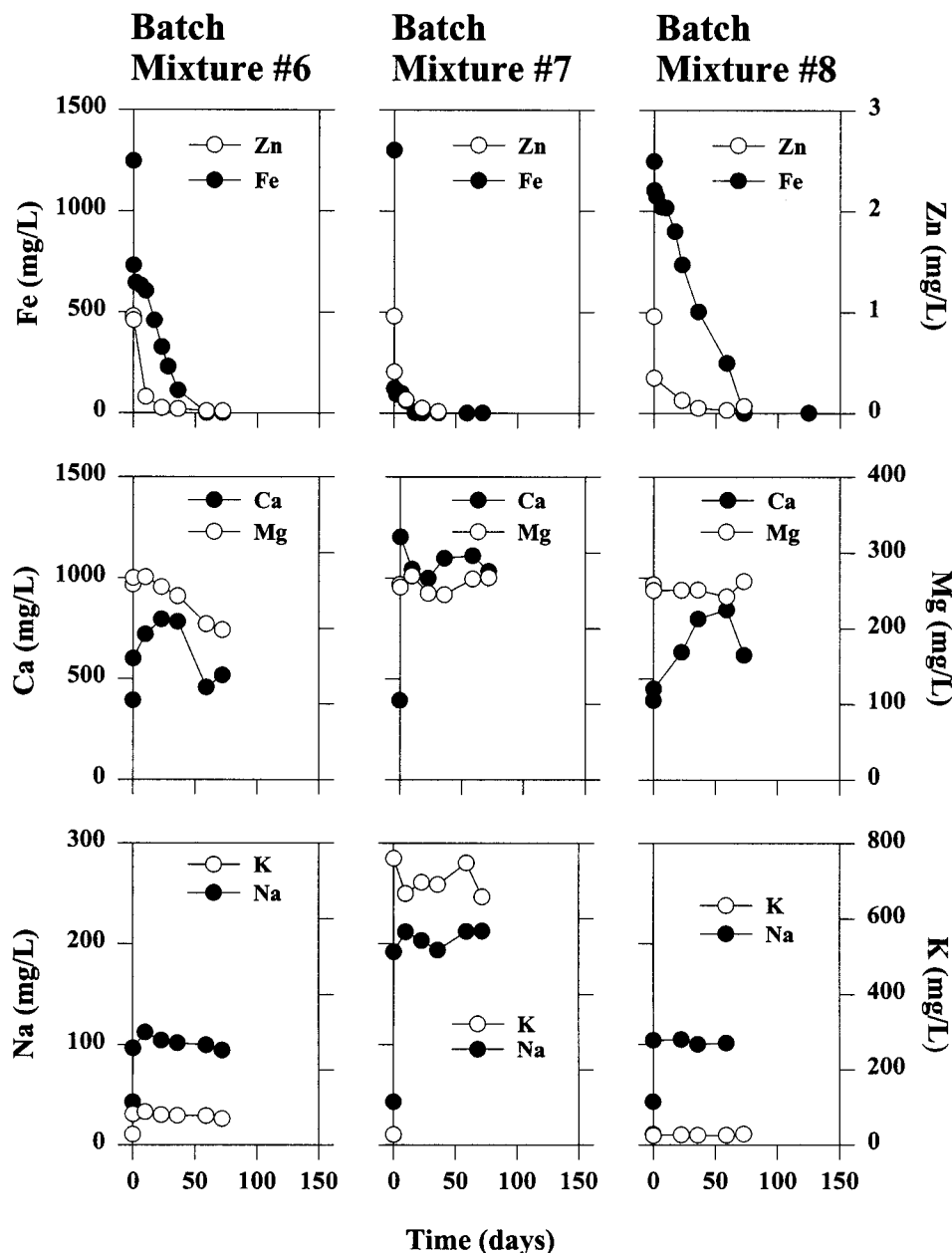
FIGURE 5. Concentrations of dissolved Fe, Zn, Ca, Mg, Na, and K for batch mixtures 6—8 as a function of time.

concentrations then decreased from between 700 and 800 mg/L to 500 mg/L in the batch mixture containing leaf mulch and sawdust (mixture 6). The initial increase in Ca is attributed to the dissolution of $CaSO_4$ added to the creek sediment. The decrease observed in mixture 6 may be due to calcite precipitation as alkalinity and pH increased over time.

Additions of Simulated Mine-Drainage Water and Metal Spikes. A second addition of simulated mine-drainage water, added to the batch mixtures containing leaf mulch (mixture 3), sheep manure, sawdust and leaf mulch (mixture 4), everything but cellulose (mixture 5), and leaf mulch, wood chips, sewage sludge and sawdust (mixture 7), indicated continued removal of SO_4 although at a 30—60% lower sulfate-reduction rate (Table 3 and Figure 6). Iron concentrations decreased from between 350 and 600 mg/L to <10 mg/L in 20—60 days. The metal spiked, simulated mine water added to batch mixture 7 contained elevated concentrations of Zn, Pb, Cd, and Ni. These metals, with concentrations as high as 480 mg/L Ni and 135 mg/L Cd, were decreased by over

99% to 0.03 mg/L and 0.01 mg/L, respectively, within 2 weeks. Concentrations of Zn were decreased from 2.3 mg/L to <0.1 mg/L, and Pb concentrations went from 0.8 mg/L to below detection (<0.015 mg/L) within 2 weeks. These results indicate the potential for continued removal of sulfate and high concentrations of dissolved metals.

Geochemical Modeling. Calculated SI values indicate that the sample water in batch experiments 6—8 approached or attained saturation with respect to rhodochrosite ($MnCO_3$), sphalerite (ZnS), mackinawite ($FeS_{0.9}$), and FeS, suggesting the carbonate phase, rhodochrosite, controlled the concentration of Mn and the sulfide phases, sphalerite, mackinawite, and FeS controlled the concentrations of Zn and Fe (Figure 7; mixtures 7—8 not shown). Initially the batch sample waters were slightly supersaturated with respect to siderite ($FeCO_3$) but over time became undersaturated, suggesting a tendency to dissolve (Figure 7). This shift from supersaturation to undersaturation occurred after the sample water became saturated or supersaturated with respect to the sulfide phases mackinawite and FeS, suggesting that SO_4 reduction and

TABLE 3. Calculated Sulfate-Reduction Rates for Batch Mixtures

batch mixture	spike[a]	sulfate-reduction rate (mg L^{-1} day^{-1} g^{-1})[b]	n	r[2]
1	1	−0.14	5	0.91
3	1	−2.15	6	0.98
4	1	−0.76	4	1.00
5	1	−4.23	4	0.99
6	1	−1.52	5	0.97
7	1	−1.69	6	0.98
8	1	−1.18	5	0.98
3	2	−1.19	6	0.99
4	2	−0.44	4	0.98
5	2	−1.70	5	0.98
7	2	−1.15	7	0.97

[a] Number of additions of solution containing metals and sulfate. [b] Sulfate-reduction rates were calculated using least squares regression analysis disregarding early- and late-time data. Also included is the number of samples used in the regression equations (n) and the correlation coefficient (r[2]). Negative values indicate removal or loss. Rates are expressed per gram of dry organic matter.

TABLE 4. Total N, P, and C Contents for Various Organic Carbon Sources Expressed as Dry Weight Percent (wt %)

organic source	nitrogen (wt %)	phosphorous (wt %)	carbon (wt %)
sewage sludge	0.38	0.57	9.3
leaf mulch	1.63	0.26	35.1
wood chips	0.09	0.01	47.4
sheep manure	0.765	0.69	11.2
sawdust	0.18	0.01	47.3
cellulose	0.01	0.00	39.9
creek sediment	0.18	0.06	3.86

TABLE 5. Aqueous Concentrations of NH_4, o-PO_4, DOC, and SO_4 Over Time for Batch Mixtures 4 and 5

mixture	days	NH$_4$ (mg/L)	PO$_4$ (mg/L)	DOC (mg/L)	SO$_4$ (mg/L)
4	0.0	<0.30	<0.15	3	1400
	0.1	22.0	19.9	98	1400
	0.9	N/A[a]	N/A	N/A	1300
	13.7	<0.3	188.3	200	1200
5	0.0	<0.3	<0.15	6.5	4000
	0.3	8.3	N/A	240	3200
	4.0	N/A	1.4	N/A	3600
	7.2	234.0	N/A	455	3500
	21.1	13.7	N/A	125	1500
	31.00	<0.3	0.8	240	30

[a] N/A = not analyzed.

metal-sulfide precipitation were the reactions controlling Fe removal at later times. Concentrations of Fe decreased over time in batch mixtures 6–8, which supports the hypothesis of Fe removal by metal sulfide precipitation reactions (Figure 7).

In all three batch mixtures, the sample water was initially supersaturated with respect to the mineral phase, greenockite (CdS), close to saturation with millerite (NiS), and undersaturated with the carbonate phases, otavite (CdCO$_3$), and NiCO$_3$. Over time, the SI values for greenockite approached saturation, millerite became more positive, and SI values for otavite and NiCO$_3$ became more negative (Figure 7). These observations, coupled with increased H$_2$S concentrations and decreased metal concentrations over time, suggest that the sulfide phases greenockite and millerite, or amorphous equivalents, controlled Cd and Ni concentrations (Figure 7).
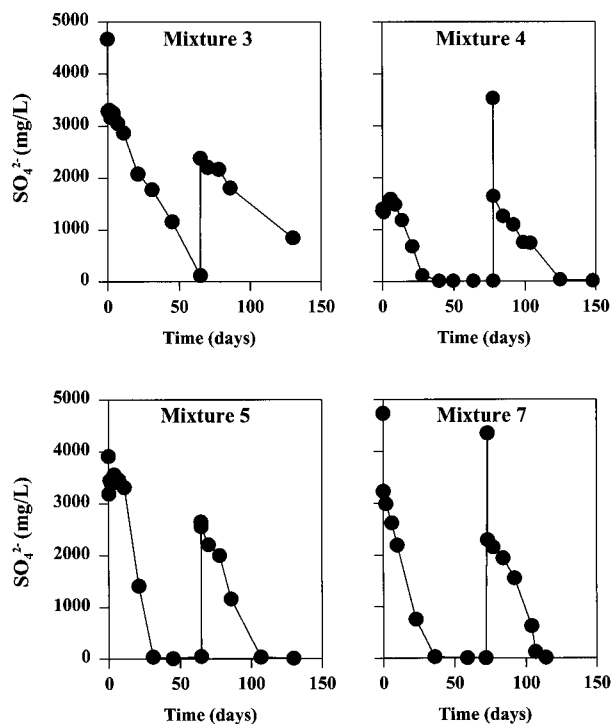
FIGURE 6. Sulfate concentrations as a function of time. A spike was added on day 65 to mixtures 3 and 5, day 78 for mixture 4, and day 73 for mixture 7.
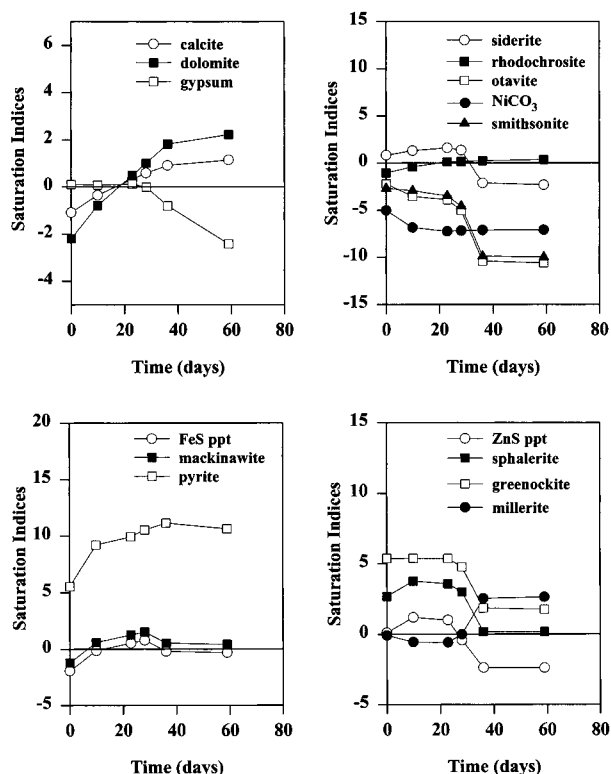

FIGURE 7. Saturation indices for selected mineral phases for batch mixture 6.

After 17 days, concentrations of Ni in the batch mixtures 6 and 7 were at or below detection and were entered as the detection limit for the geochemical calculations. After 17 days in mixture 7 and 37 days in mixture 6, the concentrations of Cd were below detection and also were entered as the detection limit.

High degrees of supersaturation for calcite and dolomite indicate a tendency for these phases to precipitate (Figure 7). The mineral structure of dolomite precludes its precipitation within most groundwater environments (30). Early time SI values for calcite and gypsum are consistent with the suggestions of Spiro and Aizenstat (31) and Krumbein (32) that high rates of sulfate reduction, as observed in mixtures 6 and 7, may lead to the precipitation of $CaCO_3$ according to the general reaction:

$$CaSO_4 + 2(CH_2O) \rightarrow CaCO_3 + H_2S + CO_2 + H_2O \quad (6)$$
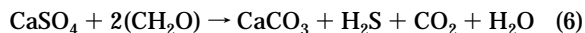
Gypsum dissolution and calcite precipitation (eq 6) can explain early time data but does not explain why SI values for calcite become more positive over time. Suess (33) found that the presence of DOC had an inhibiting effect on nucleation of $CaCO_3$, thus preventing the precipitation of $CaCO_3$. Berner et al. (34) found pore water affected by SO_4 reduction to be supersaturated with respect to calcite. Concentrations of DOC of mixture 7 sample water fluctuated between 70 mg/L and 600 mg/L. These values suggest that Ca concentrations may have been affected by the inhibition of calcite precipitation during most of the experiment.

Extensive contribution of DOC to the measured alkalinity (expressed as mg/L $CaCO_3$) may account for the high SI values observed for calcite and dolomite. Assuming that all of the measured DOC contributed to alkalinity as propionate, the DOC could have contributed up to 20% of the measured alkalinity after sulfate-reducing conditions were established. Geochemical calculations based upon these adjusted values of alkalinity resulted in little change in SI values.

Permeability of Reactive Mixtures. The permeability of the reaction mixture is an important parameter which must be considered when designing a reactive wall. The reactive mixture must be sufficiently permeable to ensure that the groundwater flows through the wall, so that treatment of the groundwater can occur. Thus, mixtures should be designed such that the permeability is the same as, or slightly greater than, that of the surrounding aquifer material.

The permeability of the reactive mixtures ranged from $>10^{-3}$ cm/s in mixtures 4 (sheep manure, sawdust, and leaf mulch) and 7 (leaf mulch, wood chips, sewage sludge, and sawdust) to $>10^{-4}$ cm/s in mixtures 3 (leaf mulch), 5 (without cellulose), and 6 (leaf mulch and sawdust). Batch mixture 8 (cellulose) was $\ll 10^{-4}$ cm/s. Required permeabilities greater or lower than those listed can be modified by altering the grain size of the organic source or by the addition of pea gravel.

Acknowledgments

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