Treatment of Metal-Contaminated Water Using Bacterial Sulfate Reduction: Results from Pilot-Scale Reactors

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Simple anaerobic reactors were installed to treat metal-contaminated water in an underground coal mine and at a smelting residues dump in Pennsylvania. The reactors consisted of barrels and tanks filled with spent mushroom compost, within which bacterial sulfate reduction became established. Concentrations of Al, Cd, Fe, Mn, Ni, and Zn were typically lowered by over 95% as contaminated water flowed through the reactors. Cadmium, Fe, Ni, and some Zn were retained as insoluble metal sulfides following their reaction with bacterially generated H_2S. Aluminum, Mn, and some Zn hydrolyzed and were retained as insoluble hydroxides or carbonates. Reactor effluents were typically circumneutral in pH and contained net alkalinity. The principal sources of alkalinity in the reactors were bacterial sulfate reduction and limestone dissolution. This article examines the chemistry of the reactor systems and the opportunities for enhancing their metal-retaining and alkalinity-generating potential. © 1992 John Wiley & Sons, Inc.

Key words: Bacterial sulfate reduction • limestone dissolution • anaerobic reactors • heavy metal sulfides • spent mushroom compost

INTRODUCTION

Bacterial sulfate reduction has been identified as a potentially valuable process for removing contaminant metals from coal and metal-mine drainage.[6,7,9,11] Under anaerobic conditions, sulfate-reducing bacteria oxidize simple organic compounds (such as lactic acid) with sulfate and thereby generate hydrogen sulfide and bicarbonate ions:

$$3SO_4^{2-} + 2 \text{ lactic acid} \rightarrow 3H_2S + 6HCO_3^- \quad (1)$$

Hydrogen sulfide reacts with many contaminant metals to remove them from solution as insoluble metal sulfides:

$$H_2S + M^{2+} \longrightarrow MS(s) + 2H^+ \quad (2)$$

where M includes metals such as Cd, Fe, Pb, Ni, and Zn. Bicarbonate ions react with protons to form CO_2 and water and remove acidity from solution as CO_2 gas:

$$HCO_3^- + H^+ \longrightarrow CO_2(g) + H_2O \quad (3)$$

The H_2S and HCO_3^- formed during sulfate reduction equilibrate into a mixture of H_2S, HS^-, S^{2-}, CO_2, HCO_3^-, and CO_3^{2-}. If sufficient sulfate reduction occurs, this mixture will buffer the solution pH to a particular value, typically in the range of 6–7, but this differs depending on the specific quantities and types of organic end-products formed. Raising the pH of acidic water will cause some metals to hydrolyze and precipitate as insoluble hydroxides or oxides[10]; for example,

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3(s) + 3H^+ \quad (4)$$

The U.S. Bureau of Mines experimented with simple water treatment reactors consisting of carboys and columns filled with organic material in which sulfate reduction became established. These reactors lowered iron, manganese, and nickel concentrations in synthetic mine drainage by 60–99% (Hammack and Edenborn).[5] These results led us to construct pilot-scale reactors of a similar design to evaluate their potential for treating metal-contaminated water. The design of these sulfate reduction reactors required

1. the exclusion of oxygen;
2. a source of sulfate (commonly present in contaminated water);
3. a source of simple organic compounds to serve as a bacterial carbon source;
4. the presence of sulfate-reducing bacteria, either indigenous to the organic carbon source or introduced; and
5. a way to physically retain metal sulfide precipitates.

Low pH (<5–6) inhibits sulfate reduction activity[12] and increases the solubility of metal sulfides. Therefore, it was also necessary to design and operate the reactors so that sufficient alkalinity could be generated to raise the pH of acidic inflows.

In this article, we present our initial findings on the performance and chemistry of the pilot-scale sulfate reduction reactors and discuss some strategies for enhancing their performance.

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MATERIALS AND METHODS

Two pilot-scale reactor systems were constructed in 1990. The reactors in each system consisted of either capped barrels (Pittsburgh system) or covered tanks (Palmerton system) filled with loosely packed spent mushroom compost. Spent mushroom compost consists of a composted mixture of manure, hay, straw, corn cobs, and wood chips that has been conditioned with gypsum and limestone and used for cultivating mushrooms. Since it decomposes readily, the compost serves as a source of organic carbon for bacterial sulfate reduction, and its bulk form serves to physically retain precipitated solids. The different mushroom composts used in each system contained 50–60 wt % organic matter and 10–15 wt % pulverized limestone.

The Pittsburgh reactor system was installed to treat acidic, iron-contaminated drainage within the experimental mine at the U.S. Bureau of Mines, Pittsburgh Research Center. This system consisted of three 200-L reactor barrels that were plumbed in series and received water from a 1140-L reservoir tank (Fig. 1a). Barrels were used instead of a single large reactor because of height limitations within the coal mine. The underground location of this system maintained a nearly constant temperature of 10°C, permitting operation during the winter.

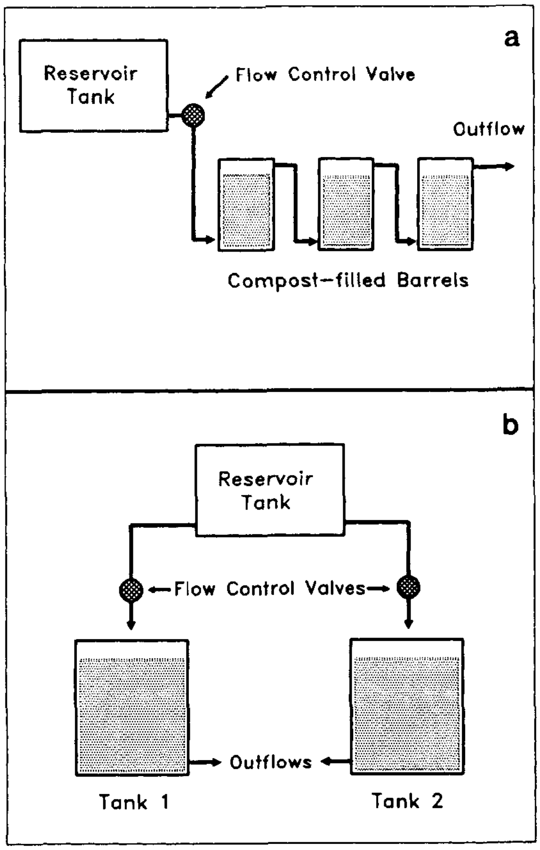

Figure 1. Schematics of (a) Pittsburgh and (b) Palmerton reactor systems.

The Palmerton reactor system was installed to treat metal-contaminated drainage from a smelting residues dump at the former New Jersey Zinc Company plant in Palmerton, Pennsylvania. This system consisted of two independent, 4500-L reactor tanks that received water from a 3500-L reservoir tank (Fig. 1b). The data presented for this system were collected during the summer and fall, when average ambient temperature ranged between 18 and 24°C.

Table I shows the quantity of compost contained in each system and the mean flow rates and residence times for each system. Because our primary objective was to evaluate the water treatment potential of the reactor systems, we used conservative residence times that previous experience with laboratory-scale reactors had indicated would result in a substantial removal of metals (data not shown). In the Palmerton system, the flow rate through one reactor (tank 2) was doubled after 10 weeks of operation to determine the effects of a shortened residence time.

Water Sampling and Analysis

Influent and effluent samples were collected at 1–2 week intervals. Samples for metals analysis were acidified immediately upon collection (total metals) or following filtration through a 1.2-μm glass fiber filter (dissolved metals). Metal concentrations were determined using an ICP atomic emission spectrophotometer, except for cadmium, which was determined using atomic absorption spectrometry. Ferrous iron was speciated by titration with $K_2Cr_2O_7$[4] using an auto-titrator in the fixed increment addition mode and a platinum redox electrode for first-derivative endpoint detection. Dissolved sulfide was determined using a Ag/Ag_2S electrode on samples treated with NaOH, and sulfate was measured using a liquid chromatograph coupled with a conductivity detector[1] following adjustment of sample pH to 8 with $NaHCO_3$. Alkalinity was determined by titration with 0.2N H_2SO_4 to pH 4.8, and acidity was determined by titration with 0.1N NaOH to pH 8.3, following boiling with H_2O_2. Whenever possible, dissolved sulfide, alkalinity, and pH were determined on the same day the samples were collected.

Table I. Selected physical characteristics of reactor system design and operation.

Characteristic	Pittsburgh system	Palmerton system Tank 1	Palmerton system Tank 2
Compost volume, L	624	3038	3038
Compost dry mass, kg	68	572	572
Flow rate, mL/min	55 (500 max)	70	70/131[a]
Residence time,[b] days	5 (0.6 min)	17	17/9[a]

[a] Flow rate increased and residence time decreased after 10 weeks operation.

[b] Within the pore space of the compost.

Compost Sampling and Analysis

The spent mushroom compost used in each system was sampled before being placed in the reactors and at irregular intervals thereafter. The final samples for the period considered in this article were collected following 54 weeks of operation for the Pittsburgh system and 18 weeks for the Palmerton system. These final samples were collected from depths of 10 and 60 cm in each barrel of the Pittsburgh system (maximum depth 75 cm) and from a depth of 60 cm at two locations in each tank of the Palmerton system (maximum depth 135 cm). At each depth or location, a composite sample of three to six subsamples was collected by hand and sealed immediately in an argon-filled container.

Compost moisture content was determined by drying subsamples to constant weight at 112°C. The total content of inorganic cations and anions was determined by ashing subsamples in a muffle furnace at 550°C for 6 h and analyzing a 12*M* HCl extract of the ash. The acid-soluble metal content was determined by extracting subsamples with 4*N* HCl under an argon sparge and analyzing this extract for metals. This acid-soluble metal content was expected to be soluble under reducing and acidic conditions and to be available for reaction with H_2S. Two subsamples from the 10-cm depth in the first reactor barrel of the Pittsburgh system were examined by Mossbauer spectroscopy[13] to directly identify the iron minerals present.

Acid-volatile sulfide (AVS), present as monosulfides such as FeS and ZnS, and chromium-reducible sulfur (CRS), present as pyrite (FeS_2) and elemental sulfur (S^0), were determined by anoxic acid distillation.[3] The sulfur was released as H_2S using 6*N* HCl and trapped in 0.2*N* NaOH. The AVS distillation solubilized 99–100% of the total content of Mn, Ni, and Zn.

Data Computation and Analysis Methods

Rates of influent loading, removal, and generation for various parameters were calculated on the basis of total reactor volume from daily or weekly averages as follows:

$$gX/m^3 \text{ day} = (g/L\,X)\,(L/\text{day flow})\,(0.62\ m^3/\text{system})^{-1} \tag{5}$$

where X represents an influent parameter or the change in a parameter. Acidity neutralization was examined by computing *alkalinity generation,* equal to the net effluent alkalinity minus the net influent acidity.

The extent to which reactor effluents were saturated with respect to solid mineral phases at chemical equilibrium was assessed using the geochemical computer program WATEQ.[2] Input to this program consisted of temperature, redox potential (E_h), and ion concentrations for typical effluent samples. The program computed equilibrium ionic activities from this input and used an internal database to generate output consisting of the ratios of the ion activity product to the solubility product constant (K_{sp}) for various minerals. Effluent E_h was estimated from the sulfate/sulfide couple[10] and was varied by ±100 mV during replicate runs of the program to assure that its inaccuracy did not influence the conclusions.

RESULTS

Both reactor systems underwent an initial phase following start-up during which Ca, Mg, Na, K, and sulfate ions were leached from the compost. By the time this phase was completed, effluent color had changed from dark brown to yellow; the effluent had acquired a strong hydrogen sulfide odor; effluent concentrations of magnesium, sodium, and potassium had fallen to influent levels; and net sulfate consumption (reduction) and metal retention were detectable. The initial leaching phase was complete after approximately 4000 L of water had passed through each reactor; this took place within 4 weeks for the Pittsburgh system and 6 weeks for the Palmerton system.

The following results pertain to system performance during the first year of operation, following the initial leaching phase described previously. For the Pittsburgh system, a 50-week period involving 16,200 L of flow is considered, and for the Palmerton system, a 16-week period involving 11,100 L (tank 1) to 19,400 L (tank 2) of flow is considered.

Changes in Water Chemistry

Mean analyses for influent and effluent water samples are shown for the Pittsburgh system in Table II and for the Palmerton system in Table III. Both systems lowered contaminant metal concentrations, usually by greater than 95%, lowered sulfate concentrations by about 20%, and produced circumneutral pH effluents having high alkalinity. Figures 2 and 3 show the rates of Fe removal by the Pittsburgh system and of Zn and Mn removal by the Palmerton system. The effluents from both systems contained high concentrations of dissolved sulfide (HS^- and H_2S), which, coupled with the lowering of sulfate concentrations, indicates that bacterial sulfate reduction was occurring.

Table II. Mean chemical analysis of influent and effluent from the Pittsburgh system.

Parameter	Influent	Effluent
pH	3.2	6.4
Alkalinity, mg/L, as $CaCO_3$	0	349
Acidity, mg/L, as $CaCO_3$	201	15
Ferrous Fe, mg/L	25	8
Ferric Fe, mg/L	28	0
Al, mg/L	7	0
Ca, mg/L	309	445
Sulfate, mg/L	1002	831
Aqueous sulfide, mg/L	0	30

Values are means of 36 influent and 27 effluent samples.

Table III. Mean chemical analysis of influent and effluent water from the Palmerton reactor system.[a]

Parameter	Influent	Effluent
pH	6.2	7.1
Alkalinity, mg/L, as $CaCO_3$	17	1583
Acidity,[b] mg/L, as $CaCO_3$	520	1
Zn, mg/L	317	0.3
Mn, mg/L	26	0.5
Ni, mg/L	0.9	0.02
Cd, mg/L	0.3	0.003
Ca, mg/L	273	700
Sulfate, mg/L	2997	2387
Aqueous sulfide, mg/L	0	109

[a] Values are means of 26 influent and 16 effluent samples.

[b] Calculated assuming that 100% of the Zn and 75% of the Mn hydrolyze at pH 8.3.

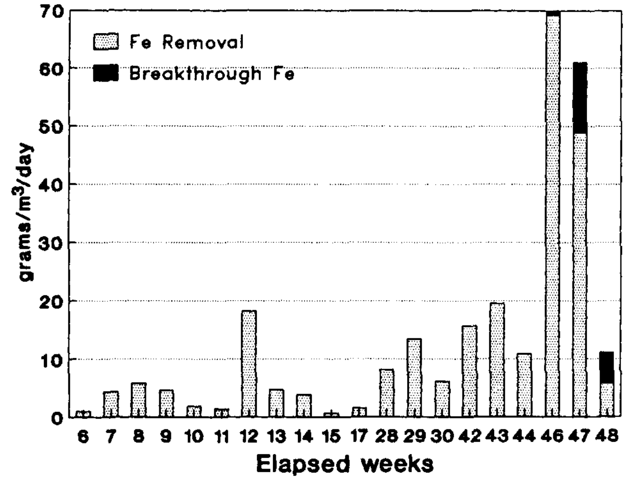

Figure 2. Iron removal rates for the Pittsburgh system, showing breakthrough iron for the 3 weeks when iron was detected in the effluent.

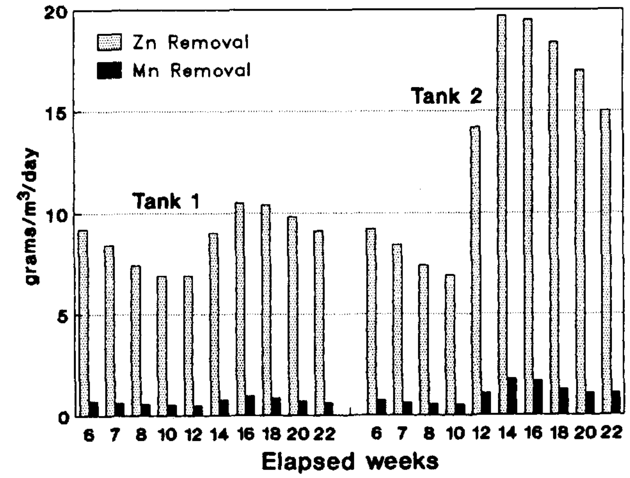

Figure 3. Rates of zinc and manganese removal for the Palmerton system.

Both reactor systems continued to release calcium after leaching of the other base cations had ceased. This calcium probably originated from the dissolution of limestone, a constituent of spent mushroom compost. Gypsum ($CaSO_4$), another major calcium-containing ingredient of mushroom compost, would probably have been depleted by dissolution during the initial leaching phase. The effluents from both systems were saturated with respect to both $CaCO_3$ and $CaSO_4$.

The Pittsburgh system consistently lowered aluminum concentrations to less than 0.2 mg/L. Since aluminum does not form a stable sulfide in the presence of water, this removal likely resulted from its hydrolysis to insoluble $Al(OH)_3$, as shown previously in Equation (4). In agreement with this, the effluent from the Pittsburgh system was found to be saturated with respect to $Al(OH)_3$. Ferric iron also hydrolyzes at circumneutral pH, but in the anaerobic environment within the Pittsburgh system barrels it was reduced to ferrous iron, which requires a higher pH for hydrolysis. Ferric iron was never detected in the effluent from the first reactor barrel, even when that barrel received an influent containing only ferric iron and was not lowering the total iron concentration. This iron reduction probably occurred in conjunction with the microbial oxidation of organic compounds (such as lactic acid) produced during the fermentation of organic matter:

$$12Fe^{3+} + \text{lactic acid} + 3H_2O \longrightarrow 12Fe^{2+} + 3CO_2 + 12H^+ \quad (6)$$

High influent loads of acidity and metals decreased the effluent concentrations of alkalinity and dissolved sulfide. For example, doubling the flow rate through tank 2 of the Palmerton system decreased effluent concentrations of alkalinity by greater than 75% and dissolved sulfide by greater than 99%. Similarly, a sevenfold increase in the influent iron load to the Pittsburgh system decreased effluent concentrations of alkalinity and sulfide by greater than 85% (data not shown).

Changes in Composition of the Pittsburgh System Compost

Table IV shows the results of the chemical analyses of Pittsburgh system compost. The ratios of acid-soluble Fe to AVS are $FeS_{0.8}$ for the first barrel and $FeS_{0.9}$ for the second and third barrels. These ratios are within the range that has been reported for the stoichiometry of amorphous and crystalline ferrous monosulfide (mackinawite).[8] In agreement with this determination, the WATEQ computer program indicated that the Pitts-

Table IV. Compost composition (μmol/g dry wt) for the Pittsburgh system.

		Final	
Component	Initial	Barrel 1	Barrels 2–3
Fe	63	352	306
Mn	8	1	9
Al	36	496	68
AVS	<0.1	291	271
CRS	23	176	165
Ca	1125	523	992

Metals are acid-soluble.

burgh system effluent was saturated with respect to FeS, and Mossbauer spectroscopy identified mackinawite as the predominant iron mineral present.

Very little iron was ever leached from the system, so most of the original 63 μmol acid-soluble Fe/g compost was retained within the reactors. Iron accumulated within the reactors only after AVS accumulated to molar concentrations exceeding those of the initial acid-soluble Fe. This suggests that the generated H_2S reacted with Fe contained in the compost solids in preference to that dissolved in the pore water.

Of the total reduced sulfur (AVS and CRS) accumulated within the system, an average of 34% was chromium reducible (CRS). Although the Pittsburgh system effluent was saturated with respect to pyrite (FeS_2), Mossbauer spectroscopy failed to detect this mineral in the compost, and the Fe content liberated during the CRS distillation indicated a maximum possible pyrite content of only 18% of the total CRS. This suggests that the CRS fraction consisted primarily of elemental sulfur (S^0).

The calcium content of the compost decreased during system operation by approximately 54% in the first barrel and by 12% in the second and third barrels. This decrease supports the hypothesis that limestone dissolution released much of the calcium and alkalinity generated by the reactor systems:

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^- \quad (7)$$

The mean rate of limestone dissolution was 121 mg $CaCO_3$/L of flow, as determined from the compost analysis.

Changes in the Composition of the Palmerton System Compost

Table V shows the results of the analyses of Palmerton system compost. Note that the molar concentration of total accumulated metals exceeds that of accumulated AVS. This indicates that the metals were not being precipitated exclusively as sulfides. Since the accumulated AVS can only account for 50–60% of the accumulated Zn, some of the Zn must have accumulated in some nonsulfide form. The effluent from the Palmerton system was found to be saturated with respect to CdS, FeS, NiS, ZnS, and $MnCO_3$. If it is assumed that all of the Fe and Ni accumulated as sulfides and all of the Mn accumulated as a carbonate, then an average of 63% of the Zn was retained in a nonsulfide form. The zinc mineral other than ZnS that came closest to being saturated in the Palmerton system effluent was $ZnCO_3$ ($[Zn^{2+}][CO_3^{2-}]/K_{sp}$ is 10^{-10} for tank 1 and 10^{-5} for tank 2). Although equilibrium chemistry does not predict $ZnCO_3$ precipitation from aqueous solution, it may have formed in the reactors through a direct surface reaction occurring on the limestone particles in the compost:

$$Zn^{2+} + CaCO_3(s) \longrightarrow ZnCO_3(s) + Ca^{2+} \quad (8)$$

Table V. Mean compost composition (μmol/g dry wt) for the Palmerton system.

		Final	
Component	Initial	Tank 1	Tank 2
Zn	26	325	507
Mn	6	34	23
Ni	0.9	1.2	1.5
Fe	68	80	72
AVS	<0.1	201	265
CRS	45	174	122
Ca	1992	1474	1291

Metals are acid-soluble.

The calcium content of the compost decreased during system operation by 26% for tank 1 and 35% for tank 2. The mean rates of limestone dissolution, as determined from the compost analysis results, were 2670 and 2070 mg $CaCO_3$/L of flow for tanks 1 and 2, respectively.

Chromium-reducible sulfur comprised 39 and 23% of the total reduced sulfur (CRS + AVS) accumulated in tanks 1 and 2, respectively. The Fe content liberated during CRS distillation indicates a maximum pyrite content of 45% of the total CRS.

Sulfur Budget

The results of the water and compost analyses indicated three sinks for the sulfate-S reduced in the reactors: reaction with metal ions to form monosulfide precipitates (AVS), conversion to FeS_2 or S^0 (CRS), and escape from the system in the effluent as unreacted H_2S. Figure 4 shows the relative rates of sulfate removal, iron removal, and effluent H_2S generation for the Pittsburgh system. Note that the moles of sulfur reduced as sulfate generally exceeded the sum of those retained as FeS or discharged as effluent H_2S. This would be expected if

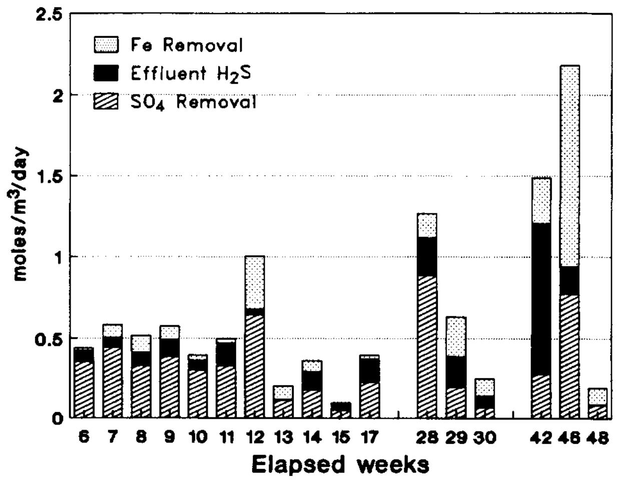

Figure 4. Rates of sulfate and iron removal and H_2S discharge for the Pittsburgh system.

iron was being retained as FeS. The sampling dates when this was not true followed periods when the system was abruptly subjected to high influent flow rates capable of forcing dissolved oxygen and ferric iron into previously anaerobic zones within the first reactor barrel. This resulted in a net production of sulfate by the first reactor barrel, probably due to the oxidation of accumulated AVS, and thereby lowered the *net* sulfate reduction rate of the system.

Figure 5 shows the relative rates of sulfate removal and Zn plus Mn removal for the Palmerton system. The moles of sulfur reduced again exceeded the moles of metal retained, except for tank 2 after the tenth week, when the flow rate was increased. Although this is consistent with the removal of the metals as sulfides, it has already been noted that all of the Mn and some of the Zn were apparently removed as carbonates. The mean difference between the removal of Mn plus Zn and the removal of sulfate was 1.0 mmol/L, which should correspond to the combined discharge of effluent H_2S and the retention of CRS, assuming that the Mn and Zn were precipitated entirely as sulfides. The actual mean effluent H_2S concentration was 3.4 mmol/L, indicating that considerable sulfide escaped in the effluent unreacted, and at least an equivalent amount of metal was removed in nonsulfide forms. Note in Figure 5 that the rate of metal removal in tank 2 increased when the flow rate increased, whereas the sulfate reduction rate remained relatively constant. This difference suggests that the reactor may have been operating near its capacity for sulfate reduction but below its capacity for carbonate formation.

Figures 4 and 5 also show the apparent rates of sulfate reduction for the Pittsburgh and Palmerton systems, assuming that all removed sulfate was reduced. The mean sulfate reduction rates were 0.333 mol/m^3 day (333 nmol/cm^3 day) for the Pittsburgh system and 0.214 mol/m^3 day for the Palmerton system.

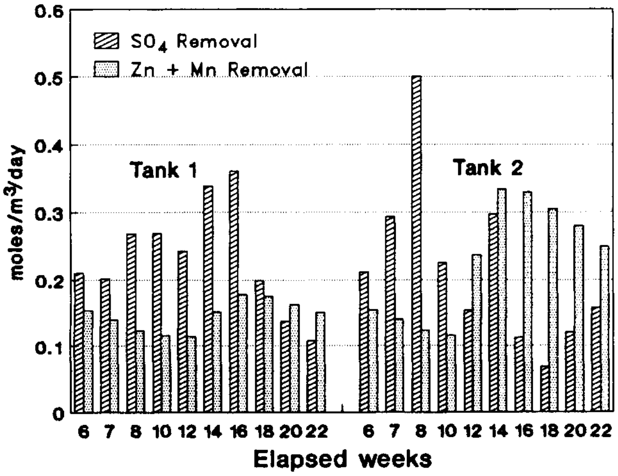

Figure 5. Rates of sulfate and zinc-plus-manganese removal for the Palmerton system.

Origins of Effluent Alkalinity

Both reactor systems consistently neutralized influent acidity and produced effluents having high net alkalinity. We hypothesized that the principal sources of this alkalinity were limestone dissolution [Equation (7)] and sulfate reduction [Equation (1)]. Each mole of calcium released by limestone dissolution and each mole of sulfate reduced should correspond to 2 equivalents of generated alkalinity. Figures 6 and 7 show the moles of calcium liberated and sulfate reduced as compared to the actual alkalinity generated (scaled for direct comparison). Linear correlation between predicted and actual alkalinity generation is high and significant for both the Pittsburgh system ($r^2 = 0.93$; $n = 17$; $P < 0.001$) and the Palmerton system ($r^2 = 0.70$; $n = 20$; $P < 0.001$). These correlations support the hypothesis that sulfate reduction and limestone dissolution were the primary sources of alkalinity in the reactor systems.

Figures 6 and 7 also indicate the mean rates of alkalinity generation and the fractions of alkalinity con-

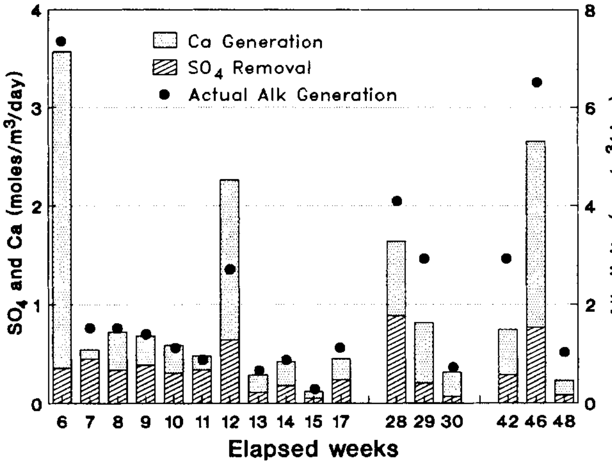

Figure 6. Rates of sulfate removal and calcium generation compared to measured alkalinity generation for the Pittsburgh system.

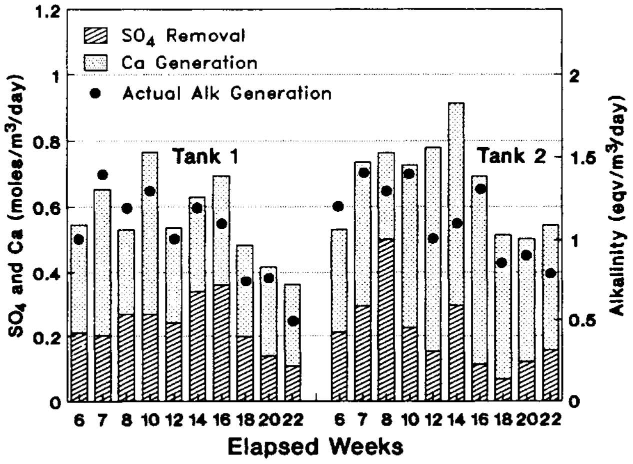

Figure 7. Rates of sulfate removal and calcium generation compared to measured alkalinity generation for the Palmerton system.

tributed by sulfate reduction and limestone dissolution. The mean rates were 2.2 and 1.1 eq/m^3 day for the Pittsburgh and Palmerton systems, respectively. Sulfate reduction contributed an average of 43% of the total alkalinity generation for the Pittsburgh system and 41 and 30% for Palmerton tanks 1 and 2, respectively.

DISCUSSION

The results presented in this article demonstrate that simple anaerobic reactors filled with bulk organic material can remove metals and acidity from contaminated water. Iron, nickel, and cadmium were retained within the reactors as insoluble monosulfides, following their reaction with bacterially generated H_2S. Aluminum and manganese hydrolyzed within the reactors and were retained as insoluble hydroxides or carbonates. Zinc was apparently retained in both carbonate and sulfide phases.

Limestone dissolution and bacterial sulfate reduction were the principal sources of alkalinity in the reactors, with the former being somewhat more important. The limestone dissolution rate generally increased in conjunction with the influent acidity load, whereas sulfate reduction was apparently inhibited once influent acidity loads rose above a certain point. This suggests that the incorporation of additional limestone into the reactors could boost the rate of alkalinity generation by both increasing the overall rate of limestone dissolution and by buffering influent acidity, thereby allowing sulfate reduction to occur uninhibited at higher influent acidity loads.

Rates of metal removal and alkalinity generation might both be enhanced in the reactors by increasing the rate of bacterial sulfate reduction. Rates of sulfate reduction and metal retention increased by a factor of 10 when lactate, a preferred carbon source for many sulfate-reducing bacteria, was added to the nickel-contaminated influent to a laboratory-scale reactor filled with spent mushroom compost[5] This suggests that the type and quantity of organic compounds released by the decomposing spent mushroom compost limit the maximum rate of sulfate reduction. Thus, the sulfate reduction rate might be increased by filling the reactors with a bulk organic material other than spent mushroom compost or by supplementing the compost by continuously adding a readily fermentable organic waste such as dairy whey or molasses to the reactors. Sulfate reduction rates might also be increased by raising the reactor temperature into the range of 25–35°C to stimulate bacterial activity.[12]

Hydraulic flow rate strongly affects performance because it determines residence time. Short residence times, such as those at which the Pittsburgh system was occasionally operated, may not allow adequate time for bacterial activity to precipitate metals and neutralize acidity. Very short residence times may also overcome the capacity of a reactor to generate alkalinity. This could result in the reactor interior being acidified to the point that bacterial activity is inhibited. On the other hand, excessively long residence times may subject a reactor to such small influent loads of metals and acidity that much of the H_2S and alkalinity produced will exit the reactor unused. This situation occurred for tank 1 of the Palmerton system, which had twice as long a residence time but only half as high a metal removal rate as did tank 2 (see Fig. 5).

The physical effects of the flow of water being treated are important considerations when designing a sulfate reduction treatment system. Since high flow rates could dislodge solids and prevent precipitates from settling, it might be advantageous to plumb several reactors in parallel rather than in series. This would disperse the flow and result in a slower flow rate through each reactor. The direction of flow through a reactor will influence the locations where gases and precipitated solids accumulate. Although water flowed upward through the Pittsburgh reactors and downward through the Palmerton reactors, no difference between the operation and performance of these systems was attributed to this difference.

The H_2S formed by sulfate reduction could present a problem if it is discharged in the reactor effluent, because of its potential toxicity and its potential to acidify the effluent by reoxidizing to H_2SO_4. Hydrogen sulfide can be removed from solution if sufficient quantities of sulfide-precipitating metals are present. However, when a substantial fraction of the influent acidity is in the form of H^+ or metals not precipitating as sulfides (e.g., Al and Mn), sulfate reduction alone cannot completely neutralize the acidity and simultaneously produce an effluent free of H_2S. It is necessary to neutralize the H^+, Al, and Mn acidity to produce an effluent free of H_2S, either by incorporating limestone into the compost or by permitting the influent to pass through a volume of limestone before entering the reactors. For example, enough limestone was present in tank 2 of the Palmerton system to neutralize the mineral acidity imparted by the Mn and some of the Zn, so that an alkaline, H_2S-free effluent was produced when a sufficient quantity of sulfide-precipitating metals entered the reactor.

Both reactor systems accumulated a considerable quantity of sulfur in the CRS fraction. In contrast with the predicted equilibrium chemistry, S^0 was the principal sulfur species present in the CRS fraction, rather than FeS_2. The formation of S^0 is important because it was reduced from sulfate at the expense of the organic materials placed in the reactors but was not exploited for the removal of metals. This S^0 was probably formed during the oxidation of H_2S by dissolved O_2 and Fe^{3+} near the interface between aerobic influent water and anaerobic, H_2S-containing pore water. Such oxidation might be minimized by avoiding variations in flow rate and influent concentrations of dissolved O_2 and Fe^{3+} that would cause the aerobic–anaerobic interface to shift position.

This study shows that acidic, metal-contaminated water can be treated using simple anaerobic reactors.

The feasibility of installing such systems to treat the discharge from industrial or mining sites will depend on system size requirements, a consideration that is presently under investigation.

CONCLUSIONS

1. Simple sulfate reduction reactors containing composted organic material as a bacterial substrate and pulverized limestone were capable of lowering concentrations of Al, Cd, Fe, Mn, Ni, and Zn by over 95% and completely neutralizing the acidity of metal-contaminated water.
2. The pilot-scale reactors accumulated Fe at rates of 5–50 g/m^3 day when operated at a residence time of 5 days and accumulated Zn and Mn at rates of 14–20 and 2–3 g/m^3 day, respectively, when operated at a residence time of 9 days.
3. Bacterial sulfate reduction and limestone dissolution were the principal sources of alkalinity in the sulfate reduction reactors and generated alkalinity at approximately equal rates in the range 0.2–2.0 equivalents/m^3 day at residence times of 5–9 days.
4. The formation of metal sulfide precipitates accounted for 36–76% of the total mass of metals retained within the sulfate reduction reactors. The formation of metal hydroxide or carbonate precipitates accounted for the remainder of the retained metals and probably was responsible for the retention of most of the Al, Mn, and Zn.
5. Approximately one-third of the sulfate-sulfur reduced in the pilot-scale reactors accumulated as elemental sulfur.

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