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The removal of nickel from mine waters using bacterial sulfate reduction

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Summary. Experiments were done to determine if a compost-based sulfate-reduction system could be used to treat nickel-contaminated mine waters. Sulfate-reduction systems were established in columns containing acid-washed mushroom compost. Simulated mine waters containing 2000 mg sulfate l^{-1} and 50–1000 mg nickel l^{-1} were adjusted to pH 4.5 and pumped through the columns at flow rates between 15 and 25 ml h^{-1}. Initially, almost all of the influent nickel was removed in the columns by sorptive and ion exchange mechanisms. The nickel removal rate then dropped to 18–30 mg nickel day (7.8 to 12.8 nmol g^{-1} compost day), where it remained relatively constant. The mechanisms responsible for the low and sustained rates of nickel removal on unamended compost are unclear. When sodium lactate was added to the inflow, sulfate reduction rates between 250 and 650 nmol day cm^{-3} compost were obtained and a sevenfold increase in the nickel removal rate was observed. The maximum nickel removal rate observed was 540 mg Ni kg^{-1} compost day (92 nmol Ni g^{-1} compost day) for columns receiving 1000 mg Ni l^{-1}.

Introduction

The sulfide-rich Duluth gabbro deposit in northeastern Minnesota may be an important future source of nickel, copper, zinc, cobalt, and associated precious metals (Rossi and Ehrlich 1990). Mining of this ore body will inevitably result in the production of contaminated water. Acidic and metal-contaminated leachates now drain from waste rock removed from a test shaft driven into a highly-mineralized zone of the deposit near Babbitt, Minn. (samples A and B, Table 1). Other portions of the Duluth Complex are being disturbed by the open-pit mining of underlying taconite orebodies, and the sulfide-rich waste rock is being stockpiled. The water quality of the drainage emanating from these stockpiles exceeds water quality standards by as much as 200 to 300 times (samples C, D, E, and F, Table 1).

Prior to mining the Duluth Complex ore deposit, water pollution control measures must be in place to ensure the protection of the region's environment. A number of options are available for the treatment of metal-contaminated drainages. Chemical treatment plants that add alkaline materials are able to treat water effectively, but they are expensive to build, maintain, and operate. Metal adsorption onto sedge peat (Eger and Lapakko 1988) and polymeric beads containing *Sphagnum* peat (Jeffers et al. 1991), are both demonstrated low-cost techniques for treating stockpile drainages with total metal concentrations of less than 100 mg l^{-1}. However, the high total metal concentrations in leachate from waste rock piles at the Babbitt test shaft (often exceeding 300 mg l^{-1}) would tend to saturate the adsorption/absorption capacity of sedge or *Sphagnum*-based treatment systems relatively quickly. The required frequency of *Sphagnum* replacement or acid stripping (in the case of peat-containing beads) could make the use of these treatment methods economically impractical.

Another potential method for the treatment of acidic Duluth gabbro leachates involves the precipitation of metals as insoluble sulfides. Crushed limestone and H_2S gas have been used previously to treat acid mine waters with a high iron content (Streeter 1970). Nickel, copper,

Table 1. Water quality of leachates from Duluth gabbro waste rock

Sample[a]	pH	Concentration (mg l^{-1})					
		SO_4^{2-}	Cu	Ni	Co	Zn	Fe
A	4.8	2740	63.0	196.0	9.1	10.3	0.10
B	4.2	3430	115.0	198.0	9.8	10.0	0.20
C	6.9	1125	0.02	1.6	0.06	0.02	0.10
D	7.2	1910	0.11	2.2	0.10	0.04	0.10
E	7.1	4000	0.64	50.0	3.4	3.6	0.10
F	5.4	1425	0.46	14.0	0.94	1.6	0.20

[a] See text for sample locations

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and many other metal ions would be expected to precipitate even more readily than iron in the presence of excess sulfides (S^{2-}, HS^-, H_2S; Ehrlich 1990). Soluble sulfide salts (e.g. Na_2S and NaHS) and sparingly-soluble metal sulfides have been used to remove Cd, Zn, Pb, and Cu as insoluble sulfides from copper smelting plant wastewaters (Bhattacharyya et al. 1979). Major advantages of sulfide precipitation over conventional hydroxide precipitation include the high reactivity of sulfides with heavy metal ions and the very low solubilities of heavy metal sulfides over a wide pH range. In addition, metal sulfide sludges are less subject to leaching under oxidizing and non-oxidizing conditions and exhibit better thickening and dewatering properties than do metal hydroxide sludges (Whang et al. 1982).

The costs of sulfide reagents used in sulfide precipitation treatment systems may be lessened by generating H_2S biologically via dissimilatory sulfate reduction. Dissimilatory sulfate-reducing bacteria reduce inorganic sulfate or other oxidized forms of sulfur to sulfide under anaerobic conditions. The overall sulfate reduction process can be represented by the generalized equation:

$$SO_4^{2-} + 2(CH_2O) \rightarrow HS^- + HCO_3^- + CO_2,$$

where CH_2O respresents a hypothetical organic electron donor that is mineralized. Sulfate-reducing bacteria vary widely in their ability to use organic compounds as electron donors, and those that are used may be either completely or incompletely oxidized (Fauque et al. 1991).

In fresh waters, bacterial sulfate reduction is often limited by the availability of sulfate ions (Herlihy and Mills 1985), but this is seldom the case in mine drainage resulting from the oxidation of sulfide minerals. Sulfate reduction activity has been detected at environmental temperatures between 0 and 92° C (Postgate 1984; Fauque et al. 1991). Bacterial sulfate reduction appears to be inhibited in acidic environments below pH 4.0 (Wakao et al. 1979). This does not preclude the metabolic activity of sulfate-reducing bacteria in acidic environments, however, because of the ability of these bacteria to generate alkalinity and buffer their immediate surroundings.

This paper investigated the potential use of bacterial sulfate reduction as a treatment method for nickel-contaminated mine drainage. Similar to chemical sulfide treatment systems, this process effectively lowers nickel concentrations in mine drainage. In addition, sulfate reduction treatment systems can generate alkalinity and lower sulfate concentrations at potentially lower operating costs.

Materials and methods

Sulfate reduction experiments were carried out in polyvinyl chloride columns (5.1 cm I.D. by 45.7 cm length) containing 400 g of mushroom compost. Mushroom compost is a waste product of mushroom farming that consists of composted straw, hay, horse and poultry manure, ground corncobs, gypsum, and limestone. As received, this material contains an intrinsic alkalinity equal to 35 tons $CaCO_3$/1000 tons. Deionized water adjusted to pH 1.0 with concentrated HCl was initially passed through the columns to remove the intrinsic alkalinity of the compost. When the pH of the column effluents dropped below 2.0, this treatment was suspended. The columns were then inoculated with leachate from fresh mushroom compost and a circumneutral solution containing 2000 mg SO_4^{2-} l^{-1} (as Na_2SO_4) was passed through the columns at a 25 ml h^{-1} flow rate for 2 weeks. After the presence of viable populations of sulfate-reducing bacteria (as growth in Postgate's medium B; McIntire et al. 1990) was demonstrated for each column, pH 4.5 solutions containing 2000 mg SO_4^{2-} l^{-1} and 50, 100, 200, 500, and 1000 mg nickel l^{-1} (as $NiCl_2 \cdot H_2O$) were passed through the columns at flow rates ranging from 15 to 25 ml h^{-1} (12 h average residence time). After 20 weeks, 3500 mg lactate l^{-1} as sodium lactate was added to the influent solutions (pH adjusted to 4.5). No effort was made to deplete the O_2 content of the influent solutions. Therefore, the dissolved O_2 content of solutions entering the columns was in equilibrium with the atmosphere, a condition likely to be encountered at most mine sites. The effluent from each column was sampled weekly and analyzed to determine pH, acidity/alkalinity, and concentrations of nickel and SO_4^{2-}. Nickel was measured by inductive coupled plasma (ICP) atomic emission spectroscopy and sulfate was measured by liquid chromatography. Acidity and alkalinity were determined by titration and expressed as mg $CaCO_3$ equivalent l^{-1}. Sulfate reduction rates were estimated based on the difference between influent and effluent sulfate concentrations and are reported with respect to compost volume. The sulfide content of column effluents was measured by a sulfide-ion-sensitive electrode when hydrogen sulfide odors were detected in effluent reservoirs.

Results

Column tests were run at influent nickel concentrations of 50, 100, 200, 500, and 1000 mg l^{-1}. Because similar results were obtained over time for all influent nickel concentrations, only those results pertaining to an influent nickel concentration of 500 mg l^{-1} are shown (Fig. 1).

Nickel removal by unamended compost

Initially, all influent nickel and some of the sulfate were removed by passage through the mushroom compost column (Fig. 1). However, nickel and sulfate removal rates and the net alkalinity of the effluent quickly decreased between the start of the experiment and day 9. The pH also decreased from 4.5 at the column influent to as low as 3.7 in the effluent during this period of time.

From day 9 to day 133, the nickel concentration in the column effluent was more constant, ranging from 425 to 465 mg Ni l^{-1} (Fig. 1). Nickel removal rates during this period ranged from 46 to 77 mg nickel kg^{-1} compost day (7.8–12.8 nmol g^{-1} compost day), or about 10% of the initial removal rate measured on day 2. The column effluent pH increased to 6.0–6.4 (Fig. 1), but there was no detectable removal of sulfate.

Nickel removal by lactate-amended compost

Results from day 161 through day 198 (Fig. 1) reflect the effects of adding 3500 mg lactate as sodium lactate to each liter of inflow. Initially (day 161), effluent nickel

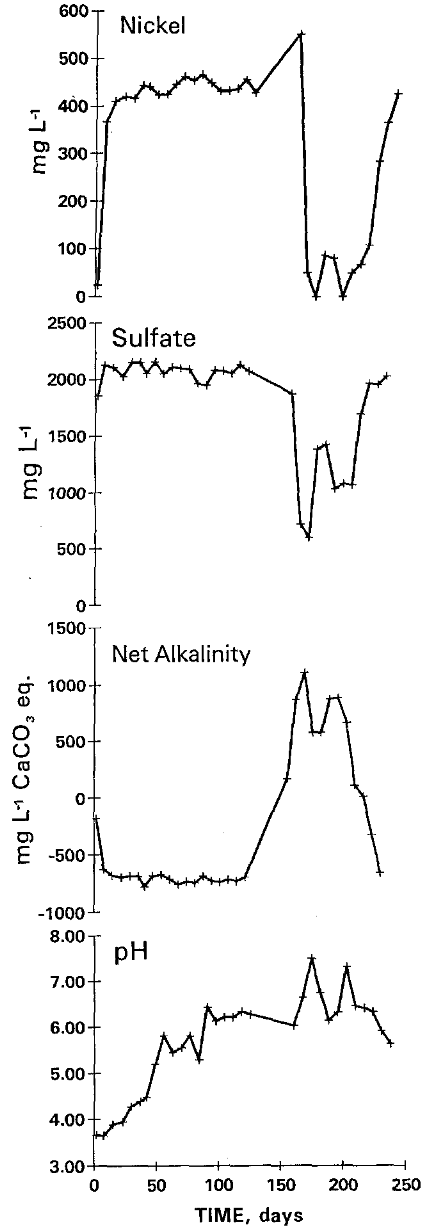

Fig. 1. Average effluent pH, nickel, net alkalinity, and sulfate concentrations from two columns receiving aqueous solutions containing 500 mg l^{-1} and 2000 mg l^{-1} of sulfate. Lactate supplementation (3500 mg l^{-1}) began on day 161 and was suspended on day 198

concentrations increased, presumably due to the displacement of nickel from ion exchange sites by sodium. By day 168, effluent nickel concentrations had decreased, averaging about 45 mg Ni l^{-1} until supplementation was suspended on day 198. The highest average nickel removal rate for the period of lactate supplementation was 540 mg Ni kg^{-1} compost day (92 nmol Ni g^{-1} compost day). When lactate supplementation was suspended, effluent nickel concentrations slowly increased to pre-supplementation levels. During lactate supplementation, column effluent sulfate concentrations dropped dramatically, and pH and alkalinity increased markedly.

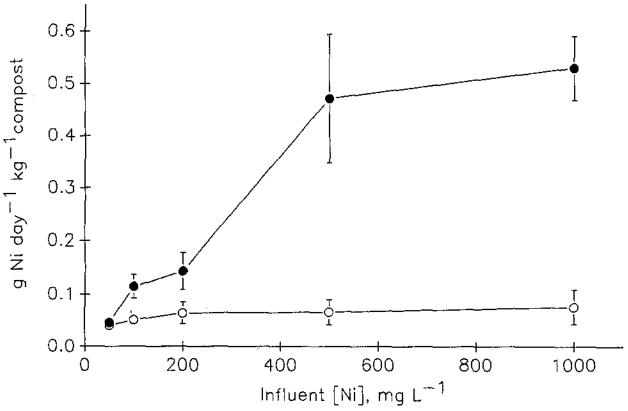

Fig. 2. Nickel removal rates (x ± SD; $n = 14$) at five influent nickel concentrations with (●) and without (○) lactate supplementation

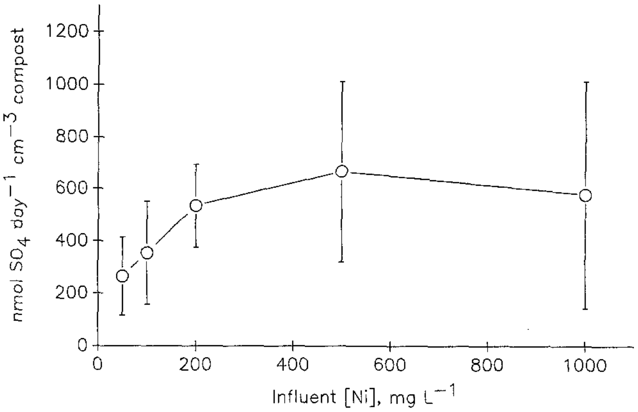

Fig. 3. Sulfate reduction rates (x ± SD; $n = 14$) at five influent nickel concentrations with lactate supplementation

Nickel removal rates for unamended and lactate-supplemented compost are shown for different influent nickel concentrations in Fig. 2. The unamended compost treatment exhibited little dependence on influent nickel concentrations, while the lactate-supplemented treatment appeared to be strongly dependent on influent nickel concentrations. These latter results are somewhat misleading because nickel loadings at concentrations less than 500 mg Ni l^{-1} were less than the maximum nickel removal rates.

Sulfate reduction rate estimates based on the rate of sulfate removal at different nickel influent concentrations are shown in Fig. 3. Sulfate reduction rates during this period ranged from 250 to 650 nmol SO_4^{2-} day cm^{-3} compost. The rates were highly variable, but the maximum rates determined were higher with increasing nickel concentration over the range of 50 to 500 mg nickel l^{-1}.

Discussion

Nickel removal by unamended compost

Sorptive mechanisms are thought to be primarily responsible for the high rate of nickel removal during the first 9 days of the experiment. The initial observed pH decrease (from 4.5 to 3.7) can be attributed to nickel displacement of H_3O^+ from ion exchange sites. Based on this pH decrease, ion exchange could account for a maximum removal of 5 mg nickel l^{-1}. Nickel removal due to ion exchange may have been higher than this, however, since some of the released H_3O^+ may have been neutralized by alkalinity produced by sulfate reduction. Because potential indicators of bacterial sulfate reduction activity, such as increases in pH and alkalinity (Fig. 1), would tend to be masked by the effects of ion exchange, the extent that sulfate reduction contributed to nickel removal could not be determined.

Both sorptive mechanisms and sulfate reduction may have been responsible for the long-term, relatively constant nickel removal from day 9 through day 161. The evidence needed to support either removal mechanism specifically was not determined in this study. For example, the continual microbial creation of sorption sites for nickel on compost could explain the observed removal rate. Likewise, the observed increase in effluent pH during this period suggested that sulfate reduction might be primarily responsible for nickel removal. However, no decrease in effluent sulfate concentration was detected. Nickel removal during this period ranged from 40 to 60 mg l^{-1}; about 65-98 mg sulfate l^{-1} would have to be reduced to precipitate this amount of nickel as a sulfide. The dissolution of residual sulfate minerals (e.g. gypsum) within the mushroom compost could have generated more sulfate than was consumed by these low rates of sulfate reduction, but this is pure speculation. No matter what processes were responsible for nickel removal during this part of the experiment, they were not responsible for a major removal of nickel, especially in comparison to the period of lactate amendment that followed.

Sulfate reduction rates in spent mushroom compost have been measured directly (McIntire et al. 1990) and inferred from the rates of metal removal or metal sulfide accumulation (Dvorak et al. 1992). These sulfate reduction rates are about 20 times greater than the hypothetical maximum rates determined for unamended mushroom compost in the present study based solely on rates of nickel removal. This is undoubtedly due to the removal of nutritional and biological components in the mushroom compost by acid-washing during column preparation. The positive response of the system to lactate supplementation alone indicates that sulfate reduction on acid-washed mushroom compost was carbon-limited. Acid-washing probably removed labile carbon available to sulfate-reducing bacteria and severely impacted the population of bacteria and fungi responsible for the degradation of more complex organic matter. Other nutrients necessary for optimal bacterial growth and activity, such as nitrogen and phosphate sources (Postgate 1984), were probably leached from the compost as well.

Nickel removal by lactate-amended compost

Sulfate reduction rate estimates during this period compare well with those measured previously in bioreactors and constructed wetlands used to treat coal and metal mine drainage (McIntire et al. 1990; Dvorak et al. 1992). These systems differed from the columns in the present study in that they contained mushroom compost that had not been acid washed, did not receive organic amendments, and did not receive nickel-contaminated influent. The similarity of rates found in all three treatment systems suggests that some characteristic common to mushroom compost, such as the surface area available for bacterial attachment, may limit the maximum sulfate reduction rates that can be attained.

Sulfate reduction rate measurements in mushroom-compost-based wetlands and bioreactors vary greatly over relatively short distances (McIntire et al. 1990), and similar conditions probably existed within the columns. Constantly changing flow paths through areas of high and low sulfate reduction activity in the columns could account for the wide fluctuation in effluent sulfate concentrations during this period.

Two factors may have led to an underestimation of the sulfate reduction rates in the compost columns. Sulfide concentrations as high as 196 mg l^{-1} were measured in column effluents (data not shown), and oxidation of some of this sulfide by O_2 would result in the production of sulfate. This oxidation reaction would also tend to be catalyzed in the presence of excess Ni^{2+} (Chen and Morris 1972). Continued gypsum dissolution might be expected to contribute some additional sulfate to the column effluent as well.

Nickel did not appear to be inhibitory to sulfate-reducing bacteria over the range of concentrations tested. In fact, average sulfate reduction rates increased slightly with increasing nickel concentration up to 500 mg l^{-1} (Fig. 3). Higher nickel concentrations in the influent may result in lower concentrations of hydrogen sulfide and bisulfide, both of which are inhibitory to sulfate-reducing bacteria at high concentrations (Miller 1950).

Conclusions

Bacterial sulfate reduction is a low-cost, low-maintenance technique capable of treating mine waters with elevated nickel concentrations. Based on 12-h residence times, sulfate reduction treatment systems containing acid-washed mushroom compost as the primary organic substrate could remove 45-75 mg nickel kg^{-1} compost day from pH 4.5 waste-waters containing up to 1000 mg nickel l^{-1}. Supplementation of the influent with 3500 mg lactate l^{-1} increased maximum nickel removal to 540 mg Ni kg^{-1} compost day (92 nmol Ni g^{-1} compost day). Other less expensive industrial organic waste products may be useful in supplementing the nutrient requirements of sulfate-reducing bacteria in environments where their metabolic activity is suboptimal. Peptone, glucose, and molasses (Wakao et al. 1979; Maree and Strydom 1987) are known to sustain sulfate reduction when fermentative bacteria are also present. Waste products of the food processing industry such as whey, brewery wort, sauerkraut filtrate, and peach peelings (Corrick et al. 1970) are low-cost supplements available in some areas. Anaerobically-digested cattle wastes (Ueki et al. 1988) have widespread availability. Research is currently underway to identify other widely-available organic waste products that can be used by sulfate-reducing bacteria and their associated fermentative bacterial populations.

Two potential drawbacks to sulfate-reduction-based treatment systems are that their efficiency will be decreased by cold temperature and by low pH. Additional capacity must be engineered into systems to compensate for reduced biological activity in winter months. Placing systems underground where temperatures are more constant may result in more uniform performance, for example. Likewise, sulfate-reduction-treatment systems could be built large enough to provide enough inherent buffering capacity to compensate for short periods of time when the influent pH would normally be inhibitory to bacteria. These engineering design alternatives are currently being investigated (Dvorak et al. 1992).

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