TRACE METAL REMOVAL FROM STOCKPILE DRAINAGE BY PEAT[1]

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Abstract.--Batch reactor tests were conducted to determine the ability of peat to remove trace metals (Cu, Ni, Co, Zn) from one acidic and two near neutral mining stockpile drainages. In all three drainages, nickel contributed 70 to 85 percent of the trace metal concentration. The sum of the trace metal concentrations in the acidic drainage was 580 mg/L at pH 3.15. At a loading of 50 g dry peat/L, 60 percent of the trace metals were removed from this drainage after one hour of reaction, with no subsequent removal. The trace metal concentrations in the near neutral drainages totaled 1.2 mg/L at pH 7.4 and 9.2 mg/L at pH 7.9. Kinetic studies on these two drainages indicated that the majority of metal removal occurred in the first 20 hours of reaction and that equilibrium was approached after about 70 hours. At a loading of 5 g dry peat/L, metal removal of 80 to 90 percent was observed for solutions maintained at pH 7.4. Trace metal removal decreased as pH decreased from 7.4 to 4.0. Release of the bound metals to distilled water at pH 7.4 was slight, and was not greatly affected by elevated concentrations of calcium, magnesium, sodium, potassium and sulfate. Metal release increased as solution pH decreased and was greater yet when the peat was exposed to bog water. Column experiments were conducted on the near neutral drainage. Metal removal from the acidic drainage was 19 mg trace metal/g dry peat.

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[1] Paper presented at the 1988 Mine Drainage and Surface Mine Reclamation Conference sponsored by the U.S. Department of the Interior (Bureau of Mines and Office of Surface Mining Reclamation and Enforcement), April 17-22, 1988, Pittsburgh, PA.

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Proceedings America Society of Mining and Reclamation, 1987 pp 291-300
DOI: 10.21000/JASMR88010291
http://doi.org/10.21000/JASMR88010291

INTRODUCTION

Five stockpiles containing low levels of metal sulfides are located at the LTV Steel Mining Company Dunka Site. Nickel concentrations in the drainages from these piles have ranged from less than 1 mg/L to nearly 40 mg/L. Concentrations of copper, cobalt, and zinc are also elevated. The Minnesota Pollution Control Agency (MPCA) recently concluded that metal concentrations in the creek draining the mine site were excessive, and in 1986 required that LTV examine means of reducing metal release from the watershed. The monthly average total concentration goals for in stream copper, nickel, cobalt and zinc were 0.030, 0.130, 0.010, and 0.047 mg/L, respectively. These values were based on United States Environmental Protection Agency (EPA) water quality criteria and other aquatic toxicity data (EPA 1980, 1984, 1986; MPCA 1988). The initial feasibility study indicated that wetland treatment may be a viable mitigation techniques for drainages with low or high trace metal concentrations.

In recent years interest has risen in the use of natural and constructed wetlands for treatment of acid mine drainage. Such applications are of particular interest in Minnesota, where peatlands cover an area of roughly 30,000 km^2. The focus of coal mine drainage treatment has been on increasing pH while reducing concentrations of acidity and iron. As mine drainage flows through wetlands, trace metals can also be removed from solution due to sequestration by peat, vegetative uptake, precipitation of metals with sulfide produced by sulfate reduction, and/or precipitation as metal hydroxides under conditions of elevated pH.

The occurrence of elevated trace metal concentrations in peat, under natural conditions, has long been recognized by geologists as an indicator of mineralization (Fraser 1961). As early as 1962 it was suggested that peat be used as a medium for removing metals from waste waters (Oreshko et al. 1962). Approximate geochemical enrichment factors (the ratio of the metal concentration in peat to its concentration in the solution with which the peat is in contact) for Cu, Ni, Co, and Zn have been reported as 2,400; 450; 6,900 and 8,600, respectively (Schnitzer and Khan 1972). Copper concentrations of 2.2 to 8.9 percent of the dry peat mass have been reported, as have nickel and zinc concentrations of 2.3 and 3.3 percent, respectively (Premi 1970, Smith et al. 1977, Szabo 1958).

The following conclusions were extracted from a literature review which addressed metal sequestration mechanisms and capacities of peat, as well as application of peat to waste water treatment (Lapakko et al. 1986). Ong and Swanson (1966) cited physical adsorption as the force which bound copper to peat. However, the majority of researchers concluded that the metal-peat bond is chemical in nature, specifying chemisorption, complexation, or chelation. It is not unlikely that both physical and chemical forces are involved in the reaction. Several researchers reported that ion exchange is involved in the reaction. To examine the sequestration of trace metals from mine drainage by peat, batch reactor and column studies were conducted. The laboratory results were compared to values observed in a white cedar swamp through which stockpile drainage flowed naturally (Eger et al. 1980).

METHODS

The peat used was a fibric, woody peat collected from the upper 0.75 m of an unimpacted black spruce bog in northeastern Minnesota. The pH of the peat was 4.5, as determined for a mixture of 15 cm^3 dry peat and 15 mL water, and the cation exchange capacity determined by the ammonium acetate method was 105 meq/100 g. Three drainages were examined, one of which was acidic (table 1). Drainage B was generated by a waste rock (0.057 pct Cu, 0.014 pct Ni) stockpile at the LTV Dunka site. The other two drainages were generated from small scale test stockpiles located near the Dunka site. The pile (FL1) generating Drainage A contained 0.35 pct Cu, 0.083 pct Ni, and 0.63 pct S. The pile (FL5) generating Drainage C contained 0.34 pct Cu, 0.084 pct Ni, and 1.41 pct S.

Erlenmeyer flasks (250 mL) covered with parafilm were used as batch reactors. A well-mixed condition was maintained by agitating the reactors on an Eberbach 6150 rotating shaker which was set at 125 excursions per minute. Kinetic experiments were conducted with 100-mL volumes of Drainages A, B, and C using peat loadings of 0.5, 1.0, and 50 g/L, respectively. Only one additional experiment was conducted with the acidic Drainage C. Metal removal was determined at seven peat loadings ranging from 0.5 to 50 g/L; solution pH was not controlled.

Experiments with Drainage A and Drainage B were more extensive. In batch reactor tests, metal removal at pH 7.4 was examined using peat loadings of 0.1 to 7 g/L. Three additional pH values, 4.0, 5.0, and 6.0, were also examined at three different mass loadings. pH was maintained by daily manual addition of NaOH or H_2SO_4 at concentrations of 1, 0.1, or 0.01 N, depending on the magnitude of adjustment required. Following the trace metal removal phase, release of metals from the solids was examined in a rinse phase with distilled water, a salt solution, and bog water. The distilled water rinse solutions were maintained at the same pH as the drainage solutions in the removal phase. The ions in the salt solution were Ca, Mg, Na, K and SO_4.

Table 1.--Composition of Drainages.

(Concentrations in mg/L unless otherwise noted.)

	Batch drainages			Column influent		Cedar swamp[1]
	A	B	C	A	B	
pH[2]	7.4	7.9	3.2	7.2-7.4[3]	7.2-7.9[3]	7.2
Cu	0.046	0.08	110	0.03	0.02	0.62
Ni	1.06	8.6	430	.86	5.4	18
Co	.029	.33	26	.05	.17	1.2
Zn	.10	.22	16	.11	.17	.38
CEU[4]	.19	1.3	180	.18	.75	3.7
Fe	NA	NA	NA	NA	NA	1.4
Mn	NA	NA	NA	NA	NA	6.5
Ca	510	300	390	270	230	280
Mg	62	142	520	26	130	220
Na	150	98	210	80	90	NA
K	50	10	34	30	8	NA
TAlk[5]	NA	NA	NA	18	51	110
TOC[6]	NA	NA	NA	10	16	22[7]

NA: not analyzed.

[1] Arithmetic mean value of stockpile drainage input over 14 months.

[2] In standard pH units

[3] Influent pH values varied over the course of the 2 to 4 month experiment.

[4] CEU = [Cu] + [Co] + 0.1 ([Ni] + [Zn]), with concentrations in mg/L.

[5] Total alkalinity as $CaCO_3$

[6] Total organic carbon as C

[7] Dissolved organic carbon.

Column experiments were conducted with these two drainages. A 2:1 mixture of wet peat to sand was required to maintain adequate flow rates in columns designed for a saturated flow rate of 5 bv/day (bed volumes per day, where one bed volume is the space occupied by the treatment hed, including voids). A saturated hydraulic conductivity of 5.4×10^{-4} cm/sec was determined for the peat-sand mixture at a dry bulk density of 1.2 g/cm^3. The peat-sand mixture in columns had a dry bulk density of 1.0 to 1.2 g/cm^3 and a porosity of 0.4 to 0.5.

Aqueous samples were filtered (0.45 micron) and analyzed for pH, sulfate, trace metals (Cu, Ni, Co, Zn), major cations (Ca, Mg, Na, K), and specific conductance. Solution pH and specific conductance were analyzed in the laboratory using an Orion 601A pH meter with a 9104 electrode and a Myron L conductivity meter, respectively. Serco Laboratories analyzed for sulfate using the barium sulfate turbidimetric technique. Metals were analyzed by atomic absorption in either the flame or flameless mode at the Minnesota Department of Natural Resources Minerals Division Office in Hibbing, MN.

RESULTS

To simplify presentation of results, the total trace metal concentration is occasionally presented in terms of "copper equivalent units" or CEU, which is calculated as:

$$CEU = [Cu] + [Co] + 0.1([Ni] + [Zn]) \quad (1)$$

This notion is based on data indicating that nickel and zinc are only one tenth as toxic as copper and cobalt (Lind et al. 1978).

A preliminary experiment was conducted to select mass loadings at which kinetic experiments would be conducted. This experiment indicated that as the peat loading increased, the solution pH decreased. For Drainage A and Drainage B the pH was reduced from 7.4 and 7.9, respectively, to about 3.7 at a peat loading of 50 g/L (dry weight). To limit the influence of peat on pH, and a potential resultant influence of pH on the kinetics of metal removal, loadings of 5 and 10 g/L were selected for Drainages A and B, respectively. The peat-induced reduction of Drainage C pH from an initial value of 3.22 was less than 0.3 units, and a loading of 50 g/L was chosen for the kinetic experiment with this drainage.

Solution pH was not controlled in the kinetic experiment, and in all cases it decreased over time. The initial pH of Drainage C was 3.1, dropping during storage from the value in the loading experiment. The pH decreased only slightly to 3.03 over 168 hours. For each trace metal, removal occurred within the first hour (fig. 1). With Drainages A and

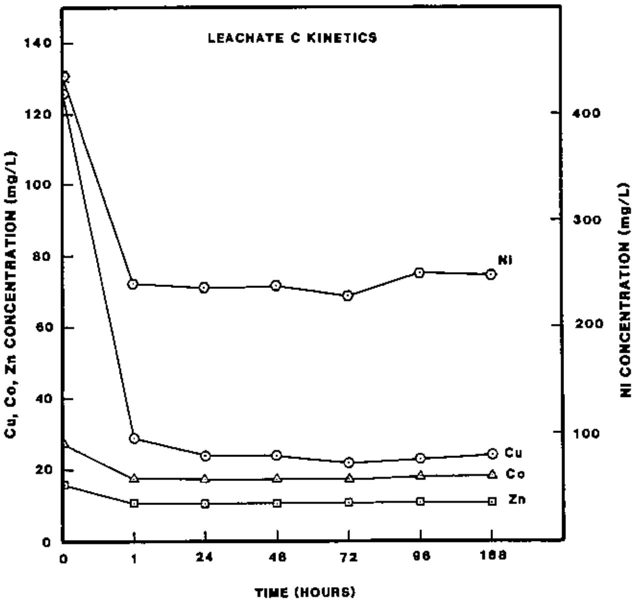

Figure 1.--Aqueous trace metal concentrations in Drainage C with a 50 g/L peat loading as a function of time.

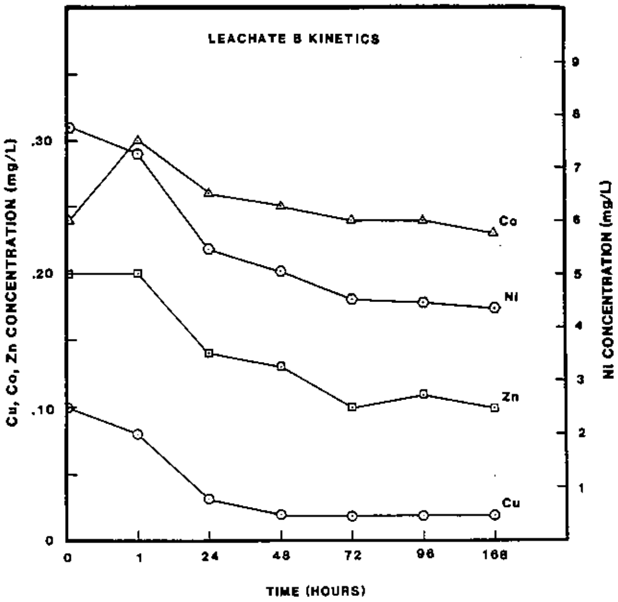

Figure 2. Aqueous trace metal concentrations in Drainage B with a 1 g/L peat loading as a function of time.

B the pH was more affected and trace metal removal was less rapid. The pH decreased from 6.9 to 5.9 with Drainage A and from 7.7 to 6.1 with Drainage B. The majority of trace metal removal from these two drainages occurred within 24 hours and little removal occurred after 48 hours (fig. 2).

Isotherm experiments, in which the peat loading was varied, were conducted on each of the three drainages. Since the pH of Drainage C did not vary greatly with peat loading, data from the preliminary loading experiment were used. Peat loadings of 0.5, 1.0, 5.0, 10, and 50 g/L were used in this experiment. Equilibrium pH values fell from 3.22 for the untreated Drainage C down to 2.95 at a peat loading of 50 g/L. There was no detectable trace metal removal at peat loadings of 0.5 and 1.0 g/L and less than 20 percent removal at 10 g/L. At the maximum loading of 50 g/L, copper removal was about 80 percent while removal of nickel, cobalt, and zinc was all about 40 percent. Mass removal of nickel was the greatest of the metals, with concentrations reduced from 430 to 280 mg/L (fig. 3). No further experiments were conducted with Drainage C.

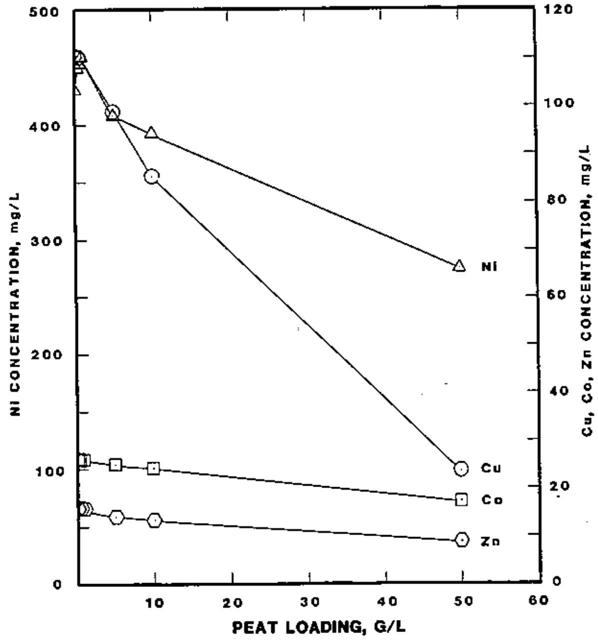

Figure 3.--Trace metal concentrations in Drainage C as a function of peat loading.

Experimentation with Drainages A and B was more extensive. To eliminate pH effects on isotherm experiments with these drainages, the pH in the reactors was maintained at 7.4 by regular addition of acid or base. With Drainage A, peat loadings of 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 g/L were used. Based on both percent and mass reduction, nickel removal was the greatest. From an initial value of 1.06 mg/L, nickel concentrations strictly decreased to 0.78 and 0.09 as the peat loading increased from 0.1 to 5.0 g/L. The copper concentration of 0.046 mg/L was reduced to 0.013 mg/L at the 0.1 g/L loading and typically remained in the range of 0.007 to 0.009 mg/L over the remaining loadings. Cobalt and zinc concentrations were fairly constant with respect to

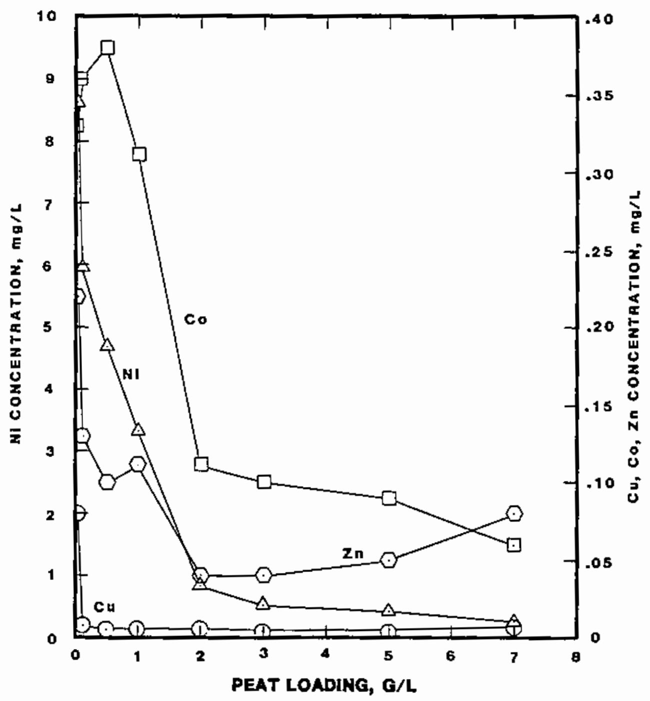

Figure 4.--Trace metal concentrations in Drainage B as a function of peat loading.

loading, with equilibrium values between 0.04 and 0.06 mg/L. There was an apparent release of cobalt to solution, but this was most likely attributable to an error in the analysis of the untreated drainage.

With Drainage B, peat loadings of 0.1, 0.5, 1, 2, 3, 5, and 7 g/L were used. From an initial value of 8.6 mg/L, nickel concentration decreased to 6.0 at the 0.1 g/L loading. Concentrations continued to decrease as loading increased and reached a minimum of 0.26 mg/L at the 7 g/L loading, a 97 percent concentration reduction. The reduction in copper concentration exceeded 90 percent at all loadings, with equilibrium concentrations in the range of 0.005 to 0.007 mg/L. The cobalt and zinc concentrations tended to decrease as the peat loading increased, with a maximum reduction of about 80 percent. The minimum observed aqueous concentrations of cobalt and zinc were 0.06 and 0.04 mg/L, respectively (fig. 4). Concentrations of calcium, magnesium, sodium, and potassium were also analyzed in this experiment. Calcium was the only one of these parameters for which removal was observed. Concentrations were reduced from 300 to 180 mg/L at the 70 g/L peat loading. Concentrations of magnesium and potassium were quite stable, typically remaining within ten percent of the initial values. Sodium concentrations increased only slightly, with an observed increase of 20 mg/L at the 7 g/L peat loading.

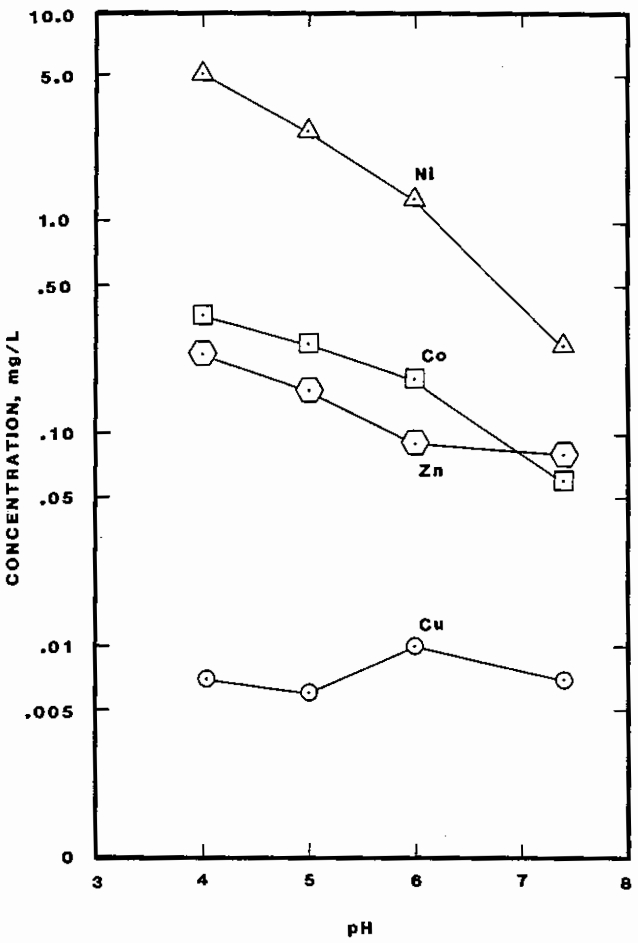

Figure 5.--Trace metal concentrations in Drainage B as a function of pH at a peat loading of 7 g/L.

The influence of pH on trace metal removal was examined in batch reactor experiments with Drainages A and B. With each drainage, three different peat loadings were exposed to drainage maintained at pH values of 4, 5, 6, and 7.4. In all cases trace metal removal decreased with decreasing pH (fig. 5). The results for equilibrium CEU levels were quantified as follows:

$$\log CEU_e = a\,(pH) + b \qquad (2)$$

The constants determined by linear regression are presented in table 2.

To determine how strongly the sorbed metals were bound, each of the solids used in the isotherm tests with Drainages A and B at pH 7.4 was placed in contact with 100 mL of distilled water and agitated as in the isotherm tests. The pH of the solution was maintained at 7.4 by regular addition of acid or base. Release from the solids to distilled water at pH 7.4 was small, typically less than five percent of the sorbed metal.

Table 2.-- Linear regression constants for log CEU_e = a pH + b[1].

Drainage A				Drainage B			
Peat Load (g/L)	a	b	r^2	Peat Load (g/L)	a	b	r^2
0.1	-0.038	-0.532	0.74	0.1	-0.047	0.38	0.64
1	- .13	- .127	.98	2	- .19	.66	.59
5	- .17	- .15	.95	7	- .28	1.11	.98

[1] CEU_e represents the equilibrium aqueous CEU concentration in mg/L.

Release tended to increase as the pH of the rinse solution decreased and as its ionic strength increased. For solids used with Drainage B, metal release at pH 4 was 2.5 to 5 times that at pH 7.4. Release to a salt solution at pH 7.4 was twice that observed for distilled water at the same pH. These trends were less pronounced for solids used with Drainage A. For both drainages, metal release to bog water at pH 4 was six to eight times the release to distilled water at the same pH.

Trace metal removal from Drainage A and B was also examined using a set of triplicate columns for each drainage. The results from each set of three columns were highly reproducible. The peat-sand mixture used in column tests with Drainage A depressed pH. Effluent values of 3.9 to 4.1 were observed, as compared to the influent pH of 7.4. With this drainage the peat-sand was replaced with a mixture of peat and low sulfur tailings (2 g wet peat: 1 g dry tailings) which produced a higher effluent pH and lower trace metal concentrations than the peat-sand mixture.

The columns containing the peat-tailings mixture reached breakthrough after 230 bed volumes (bv) of Drainage A flowed through the column at a rate of 5 bv/day. The maximum CEU reduction observed was 50 percent. The removal of individual metals tended to increase with the influent concentration (fig. 6). Removal was lowest for cobalt (essentially zero), and copper (6.3 mg/kg dry solid), and highest for nickel and zinc (85 and 11 mg/kg dry solid, respectively).

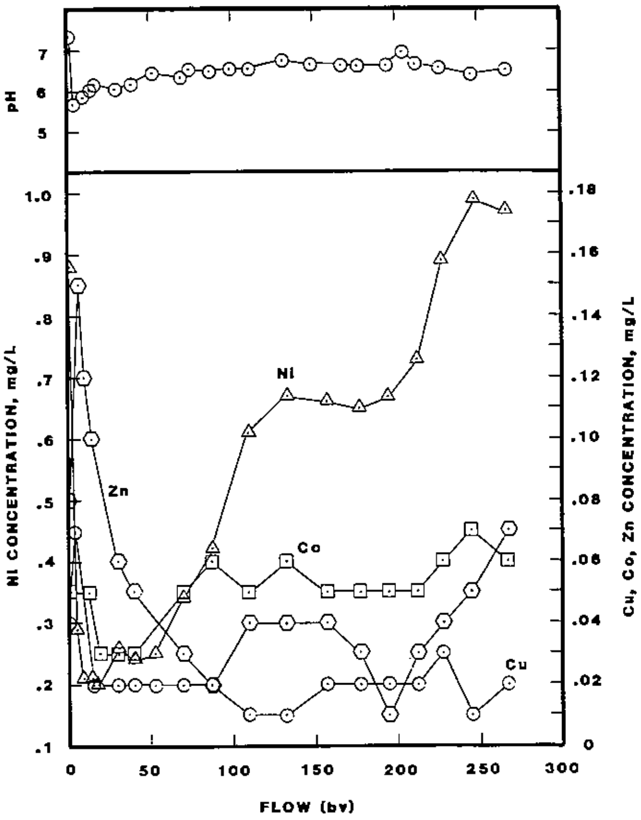

Figure 6.--Drainage A column effluent quality as a function of cumulative effluent volume.

Although the Drainage B columns did not reach total breakthrough (the point at which concentrations in the effluent equal those in the influent), the trends were similar to those observed for the Drainage A columns and in batch experiments. Metal removal was a function of trace metal concentration and increased as pH increased. The initial effluent had elevated trace metal concentrations, although less than influent levels, and depressed pH. The trace metal concentrations decreased fairly rapidly, reaching a minimum after about 25 to 35 bv of flow. Concurrent with this decrease was an increase in pH. Subsequently, the effluent CEU levels varied between 0.6 and 0.7 mg/L and pH stabilized at about 7. Some problems were encountered in maintaining flow rates, and were attributed to compaction of the peat-sand bed.

DISCUSSION

In a wetland setting, peat can provide a reasonably rapid removal of trace metals from mine drainage for an extended period. The removal kinetics are affected by drainage composition. To reach equilibrium, the peat-metal reaction required less than one hour with the acidic drainage and roughly 24 to 48 hours for the neutral drainages. The slower kinetics observed for Leachates A and B may have been influenced by several factors. First, the decreased peat loading and the lower metal concentrations would tend to slow apparent reaction rates, assuming typical relationships between rates and reactant concentrations. Secondly, dissolved organics which have leached from the peat may form soluble organometallic complexes and thereby effectively compete with functional groups on the peat for low concentrations of trace metals. Fulvic acid, for example, are present in peat and are, by definition, soluble in both acidic and basic solutions. Gamble et al. (1970) indicated that these ill-defined compounds can chelate copper. Thirdly, the influence of other cations, such as calcium, competing for binding sites on the peat would tend to be greater at low trace metal concentrations. Trace metals have a greater tendency than calcium to complex with organics. However, calcium might compete with some effectiveness since its concentration exceeded that of the trace metals by as much as four orders of magnitude. Even considering the slower rate, a retention time of 24 to 48 hours does not seem unreasonable for a wetland system treating mine drainage. A travel time of 50 days was reported for the flow of mine drainage through a cedar swamp in northeastern Minnesota (Eger et al. 1980).

The degree to which trace metal concentrations were reduced simulates the treatment efficiency in a field setting. The maximum metal removal from Drainages A and B, or treatment efficiency, typically was 60 to 97 percent of the aqueous metal. The fraction of nickel removed was greatest, while that of cobalt and zinc was the least. With Drainage C the copper removal was greatest (80 pct), while removal of Ni, Co, and Zn ranged from 35 to 40 percent.

Analyses of solution composition revealed the extent to which aqueous concentrations were reduced, but did not quantify the potential lifetime of peat in a field setting. One objective of the isotherm experiments was to generate data required for application of the Langmuir isotherm equation, and thereby determine removal capacities. With the exception of nickel, Langmuir isotherms did not describe the metal removal adequately. Similarly, Ryss and Hoffmann (1979) reported nonlinear Langmuir results for peat with Cu, Ni, Cd, and Zn. This was not totally surprising since this application of Langmurian theory assumes removal is the result of adsorption by a homogeneous surface from a simple solution. Both the peat and the drainages were complex in composition, and mechanisms other than adsorption were probably involved in removal reactions. At low concentrations, the complexation of trace metals by organics leached from the peat could have a significant influence on adsorption. The analytical error at the low concentrations, particularly for cobalt and zinc, is also greater. Since Langmurian theory did not describe the data, the theoretical removal capacities could not be calculated. Therefore, metal sequestration could be quantified only in terms of observed removal.

Wieder (1984) used the Langmuir equation to describe metal sorption onto peat, but his experimental approach differed in several aspects. First, he used a flow through system rather than batch reactors. Second, his solutions contained ferrous iron concentrations as high as 200 mg/L, as opposed to the relatively low trace metal concentrations typical of this study. Third, his solutions were prepared from ferrous ammonium sulfate, as opposed to more complex drainages used in these batch studies. Fourth, as opposed to the linear transformations used to calculate Langmuir constants in this study, he used a nonlinear technique, which appears to be superior (Rubin and Mercer 1981). More recently Wieder (1988) found that the nonlinear estimation method adequately determines the Langmuir adsorption capacity but yields questionable values for the energy of interaction for peat adsorption of metals from more complex solutions.

The mass of trace metals removed was influenced by aqueous metal concentrations and increased with increasing pH. The greatest mass removal was observed for nickel, which was the predominant trace metal in solution (table 3). Trace metal concentrations in Drainage B were higher than those in Drainage A. Similarly, trace metal removal from Drainage B, was greater than that from Drainage A. Although metal concentrations in Drainage C were higher than those in the other two drainages, the metal sequestration was not always higher. This was due in part to the pH of Drainage C, which was 4.2 units lower than that of the other drainages. The acidic conditions reduced the removal efficiency of the peat, as was verified in batch tests with Drainages A and B. This suggests that metal removal by peat in a wetland treatment system will be enhanced if the pH of acidic drainages is elevated prior to input to the wetland. Elevation of pH could also be accomplished by addition of alkaline solids to the peatland, but this could lead to chemical precipitation and possibly fouling of the peat. Ground water input to the peatland can provide some natural pH elevation.

Reduced removal at low pH was also observed in the column experiments. With Drainage A, tailings were required to neutralize the acid present on the peat. The alkalinity of Drainage B was three times that of Drainage A, and effectively neutralized the acidity of the peat. The initial effluent from both types of columns had relatively low reductions in trace concentrations and depressed pH. The pH

Table 3.--Metal binding by peat, values in mg/kg.

Metal	Batch Experiments[1] Drainage A	 Drainage B	 Drainage C	Column[2] Drainage B	Cedar swamp[3]
Cu	330	730	2,500	29	3,600
Ni	2,800	26,000	4,000	18,000	6,400
Co	2	110	300	580	3,600
Zn	200	900	200	890	270
Fe	NA	NA	NA	NA	26,000
Mn	NA	NA	NA	NA	15,000

NA: not analyzed.

[1] Maximum values observed based on reductions in aqueous concentrations.
[2] Average values for three columns; columns approached, but did not reach breakthrough. Drainage A columns excluded since it was difficult to discriminate between metal bound by peat and that bound by the tailings.
[3] Maximum observed total extractable metal concentration.

Table 4.--Geochemical enrichment factors in the laboratory and field.

Metal	Batch Experiments Drainage A	 Drainage B	 Drainage C	Column Drainage B	Cedar swamp
Cu	7,200	9,100	23	1,400	5,800
Ni	2,600	3,000	9.3	3,300	360
Co	69	330	12	3,400	3,000
Zn	2,000	4,100	12	5,200	270
Fe	NA	NA	NA	NA	19,000
Mn	NA	NA	NA	NA	2,300

NA: not analyzed.

depression was also observed in the batch experiments and was not surprising since the peat pH was 4.5. In addition to hydrogen ion equilibration between peat and water, hydrogen ions present in certain functional groups, for example carboxyl groups, would be released in ion exchange reactions involving cations in solution.

Geochemical enrichment factors (GEF, the ratio of the metal concentration in the peat to metal concentration in solution) normalized for differences in aqueous metal concentrations provided the closest simulation of field values. The GEF values calculated for the neutral drainages typically ranged between 1,400 and 7,200. The GEF values for copper and cobalt in a white cedar swamp receiving neutral mine drainage were in a similar range (table 4).

The nickel and cobalt GEF values observed in the field were lower than this range. This may be partly due to the fact that the values listed in table 4 tend to underestimate the actual GEF values. The tabulated values were calculated using the concentrations at the stockpile, which were higher than those at the site where the metal content of the peat was analyzed. Secondly, equilibrium with respect to these metals may not have been achieved in the swamp. Finally, the GEF value for zinc at the low aqueous concentrations observed in the field may tend to be aberrant. At these low concentrations there may be effective competition from aqueous phase complexing organics leached from the peat. Extremely low GEF values were also observed for cobalt in the batch tests with Drainages A and B.

Peat has been reported to sequester some trace metals preferentially over others (Bunzl et al. 1976, Ryss and Hoffmann 1979, Schmitzer and Khan 1972), and results of this study suggest that copper is preferred over nickel, cobalt and zinc. With Drainage C copper was preferentially removed, and copper concentrations in Drainages A and B were reduced to low equilibrium values at low peat loadings. The highest calculated GEF values were for copper, except in column experiments with Drainage B. In this experiment aqueous copper concentrations were very low, and the previously mentioned competition from aqueous phase organics may have been influential. Field data from other northeastern Minnesota sites indicate a preferential sequestration of copper by organics. Analysis of organic stream sediments contacting mine drainage yielded GEF values for copper, nickel, cobalt, and zinc of 25,000; 3,500; 8,300; and 3,800, respectively (Eger and Lapakko 1980).

The results of batch and column experiments indicate that solution compositional factors such as pH, metal concentration, and presence of competing metals influence trace metal removal. The composition and hydraulic conductivity of peat and wetland hydrology also influence trace metal removal. Consequently, the efficiency and capacity of peat to remove trace metals from specific drainages can be accurately assessed only on a site specific basis. Nonetheless, approximations can be used to gain some insight on the amount of metal removal a peatland can provide.

The batch and column experiments indicated that one kilogram of peat (dry weight) is capable of sequestering roughly 20 g of nickel from Drainage B, field data suggest a value of slightly more than 6 g. For this example a reasonable and convenient nickel removal capacity of 10 g/kg will be used. For field calculations removal capacity might be more appropriately expressed as 10 kilograms nickel per metric ton of peat. Assuming a peat depth of 1 m and a dry density of 0.1 tons/m^3, this implies a removal capacity of 10 tons of nickel per hectare of peatland.

In a natural peatland problems are presented by the low hydraulic conductivity of peat (Rycroft et al. 1975). Flow does not occur uniformly throughout the peat, but instead tends to occur over the surface and in the upper peat layer (Eger, et al. 1980). Consequently, it is advantageous to modify the peat layer in wetlands receiving mine drainages. Furrowing or disking the peat (perpendicular to the direction of flow) would allow the drainage to contact a greater surface area of peat and, thereby, improve metal removal. Flow through the lower layers of peat may also be enhanced by ditching perpendicular to the natural flow gradient. The effectiveness of this approach may, however, be limited by the slight gradients which are typical of natural peatlands. If peat were removed from the natural setting, the hydraulic conductivity could be increased by mixing the peat with inorganic solids, such as the sand or tailings used in the column experiments. Use of an alkaline material such as limestone, with this or other approaches, would further enhance trace metal removal by elevating pH.

Based on the desorption experiments with distilled water, the metals removed by the peat would remain tightly bound if the peat were contacted by precipitation. From 1983 through 1986 the volume weighted average precipitation pH at four sites in northeastern Minnesota ranged from 4.62 to 5.21, with a median of 4.82 (Twaroski, 1988). The degree of release would increase with decreasing pH. Indeed, it is possible that metals could be recovered from the peat when its capacity was reached. Metals could be released from the sorbed state by acidic solutions or by solutions containing strong complexing agents, as inferred by the elevated metal release to bog water. Exposing the metal loaded peat to high ionic strength solutions would also release bound metals. The batch experiments indicated that the acidic solution and bog water were superior for desorbing trace metals, but more efficient salt solutions than that used in these tests most likely exist. Another option would involve burning the spent peat, with possible attendant energy recovery, and recovering metals from the ash. The surface peat could be removed as its capacity was exhausted, thereby exposing the less taxed lower layers of peat.

SUMMARY

Laboratory studies indicate that peat is capable of reducing trace metal concentrations in mine drainage by more than 90 percent, and the reaction kinetics are adequate for peat to be a major trace metal sink in wetlands. The trace metal removal capacity is on the order of 20 g/kg, is dependent on trace metal concentrations, and decreases as pH decreases. At low concentrations, removal may be limited due to trace metal complexation by dissolved organics which leach from the peat. The batch and column data provided a reasonable simulation of trace metal removal in the field when the influence of solution composition was considered. If wetland systems are engineered to permit the contact of mine drainage with lower layers of peat, tens of tons of trace metals can be removed per hectare of peatland.

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