BuMines OFR 20A-87
PB87-186136

A mining research contract report
AUGUST 1986

LOW-COST REMOVAL OF TRACE METALS FROM COPPER-NICKEL MINE STOCKPILE DRAINAGE. VOLUME I, LABORATORY AND FIELD INVESTIGATIONS.

Contract J0205047
Minnesota Department of Natural Resources

Bureau of Mines Open File Report 20A-87

BUREAU OF MINES
UNITED STATES DEPARTMENT OF THE INTERIOR

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies or recommendations of the Interior Department's Bureau of Mines or of the U. S. Government.

PB87-186136

Low-Cost Removal of Trace Metals from Copper-Nickel Mine Stockpile Drainage
Volume 1. Laboratory and Field Investigations

Minnesota Dept. of Natural Resources, St. Paul

Prepared for

Bureau of Mines, Washington, DC

Aug 86

BuMines OFR 20A-87

PB87-186136

A mining research contract report
AUGUST 1986

LOW-COST REMOVAL OF TRACE METALS FROM COPPER-NICKEL MINE STOCKPILE DRAINAGE.

VOLUME I, LABORATORY AND FIELD INVESTIGATIONS.

Contract J0205047
Minnesota Department of Natural Resources

Bureau of Mines Open File Report 20A-87

BUREAU OF MINES
UNITED STATES DEPARTMENT OF THE INTERIOR

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies or recommendations of the Interior Department's Bureau of Mines or of the U. S. Government.

50272-101

REPORT DOCUMENTATION PAGE

1. REPORT NO. BuMines 20A-87

2.

3. Recipient's Accession No. PB87 186136/AS

4. Title and Subtitle

Low-Cost Removal of Trace Metals from Copper-Nickel Mine Stockpile Drainage. Volume I—Laboratory and Field Investigations

5. Report Date Aug. 1986

6.

7. Author(s)

Kim A. Lapakko, A. Paul Eger, and James D. Strudell

8. Performing Organization Rept. No.

9. Performing Organization Name and Address

Minnesota Department of Natural Resources
Division of Minerals
500 Lafayette Rd., Box 45
St. Paul, MN 55155-4045

10. Project/Task/Work Unit No.

11. Contract(C) or Grant(G) No.

(C) J0205047

(G)

12. Sponsoring Organization Name and Address

Office of Assistant Director--Mining Research
Bureau of Mines
U.S. Department of the Interior
Washington, DC 20241

13. Type of Report & Period Covered

Contract research, Sept. 1980-Nov. 1983

14.

15. Supplementary Notes

Approved for release Apr. 16, 1987

16. Abstract (Limit: 200 words)

This report describes a two-phase experimental program to examine the feasibility of removing trace metals (Cu, Ni, Co, Zn) from stockpile effluent using readily available materials in low-cost, low-maintenance systems. Volume I details the process, beginning with the first phase, a laboratory screening program using (1) batch experiments to screen wood chips, peat, till, tailings, zeolite, lime, and sponge iron, and (2) column experiments to select the most promising materials for field trials. Low-sulfide tailings were chosen for the second phase field testing, utilizing both treatment beds and joint disposal bins. Saturated and unsaturated flow tailings treatment beds demonstrated the greatest removal efficiency for copper (95 and 89 pct) and lowest for nickel (9 and 24 pct). A model was developed for the unsaturated bed to express output flow at a given distance from the input as a function of input flow. In the joint disposal study, total discharge from waste rock was reduced 34 pct by the addition of tailings and 66 pct by the addition of tailings followed by revegetation. The associated reductions in trace metal mass release were 73 and 87 pct, respectively. The drainage from the bins incorporating tailings had lower trace metal concentrations and higher pH than the drainage from the controls.

17. Document Analysis a. Descriptors

Mining research
- Adsorption
- Cobalt
- Copper
- Drainage
- Industrial wastes
- Ion exchange
- Joint disposal
- Lean ore
- Mining
- Nickel
- Peat
- Stockpile
- Tailings
- Till
- Trace metals
- Treatment bed
- Waste rock
- Wood chips
- Zinc

b. Identifiers/Open-Ended Terms

- Batch reactor
- Ion exchange column
- Copper-nickel
- Cu-Ni
- Heavy metals
- Mine drainage
- Mitigation
- Waste characterization

c. COSATI Field/Group

18. Availability Statement

Release unlimited by NTIS.

19. Security Class (This Report) Unclassified

20. Security Class (This Page) Unclassified

21. No. of Pages 103

22. Price

(See ANSI-Z39.18) *See Instructions on Reverse* OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

FOREWORD

This report was prepared by the Minnesota Department of Natural Resources, Division of Minerals, in St. Paul, Minnesota, under USBM Contract number J0205047. The contract was initiated under the Minerals Environmental Technology Program. It was administered under the technical direction of the Twin Cities Research Center with P. G. Chamberlain acting as Technical Project Officer. R. J. Simonich was the contract administrator for the Bureau of Mines. This report is a summary of the work completed as a part of this contract during the period September 1980 to November 1983.

CONTENTS

CONTENTS (continued)

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

bv	bed volume	L/s	liter per second
bv/d	bed volume per day	m	meter
$^{\circ}$ C	degree Celsius	m^2	square meter
cm	centimeter	m/s	meter per second
cm^2	square centimeter	meq	milliequivalent
cm/s	centimeter per second	mg/L	milligram per liter
CEU	copper equivalent unit	Mmt	million metric ton
g	gram	mt	metric ton
g/cm^3	gram per cubic centimeter	mt/m^3	metric ton per cubic meter
g/L	gram per liter	pct	percent
ha	hectare	s/cm^3	second per cubic centimeter
kg	kilogram	ug/L	microgram per liter
km^2	square kilometer	um	micrometer
L	liter	uS/cm	microsiemen per centimeter
L/d	liter per day		

LOW-COST REMOVAL OF TRACE METALS FROM COPPER-NICKEL MINE STOCKPILE DRAINAGE

by

K. A. Lapakko[1], A. P. Eger[2], and J. D. Strudell[3]

ABSTRACT

A two-phase experimental program was conducted under U.S. Bureau of Mines funding to examine the feasibility of removing trace metals (Cu, Ni, Co, Zn) from stockpile effluent using readily available materials in low cost, low maintenance systems. The first phase was a laboratory screening program using: 1) batch experiments to screen wood chips, peat, till, tailings, zeolite, lime and sponge iron; and 2) column experiments to select the most promising materials for field trials. Low sulfide tailings were chosen for the phase two field testing, utilizing both treatment beds and joint disposal bins. Saturated and unsaturated flow tailings treatment beds demonstrated the greatest removal efficiency for copper (95 and 89 pct) and lowest for nickel (9 and 24 pct). A model was developed for the unsaturated bed to express output flow at a given distance from the input as a function of input flow. In the joint disposal study, total discharge from waste rock was reduced 34 pct by the addition of tailings and 66 pct by the addition of tailings followed by revegetation. The associated reductions in trace metal mass release were 73 and 87 pct, respectively. The drainage from the bins incorporating tailings had lower trace metal concentrations and higher pH than the drainage from the controls.

---

[1] Senior engineer
[2] Principal engineer
[3] Research analyst
Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN.

INTRODUCTION

The Duluth Complex, located in northeastern Minnesota, is a massive gabbroic intrusion containing low grade copper and nickel sulfides (82).[4] These deposits represent one of the largest known copper and nickel resources in the U.S. (70, 87). The development of this resource could produce a number of environmental impacts, many of which could be due to leachate generation (67). Among the principal sources of leachate would be lean ore and waste rock stockpiles (123). Leachate generated by Duluth Complex waste rock stockpiles at the Dunka Mine, near Babbitt, Minnesota, has had Cu, Ni, Co and Zn levels 10 to 10,000 times the background levels of undisturbed streams in the area (28). These trace metals have caused adverse biological impacts at aqueous concentrations less than 10 ug/l (81).

Development of the Duluth Complex copper-nickel deposits would require extensive open pit mining which, based on conceptual mining models, could produce an estimated 4 to 10 square kilometers of waste rock stockpiles, depending on the stripping ratio and stockpile height (119, 128, 130). The estimated volume of drainage generated by stockpiles of this size would be 1.5 to 3.8 billion liters in a year of average precipitation (56). Means of mitigating the adverse environmental impacts of this drainage, particularly those related to elevated trace metal concentrations, may be required for resource development. If mitigation is required after mining has ceased, the use of low cost, low maintenance methods would be advantageous.

The U. S. Bureau of Mines provided funding to the Minnesota Department of Natural Resources (DNR) Division of Minerals, to investigate the use of low cost materials in a low maintenance treatment system for removing trace metals from copper-nickel mine stockpile drainage. The first phase of the project was a series of laboratory batch and column tests carried out at the DNR lab in Hibbing and at facilities provided by the Mineral Resources Research Center (MRRC) on the Minneapolis campus of the University of Minnesota. Batch tests were conducted with wood chips, peat, till, and copper-nickel tailings to select materials for column tests. For purposes of comparison, zeolite and lime were included in the batch tests, and sponge iron was examined for both treatment and metal recovery. The column tests were used to select materials for the second phase of the project. In this phase, field tests were conducted to examine: 1) the effectiveness of tailings treatment beds under both saturated and unsaturated flow conditions; and 2) the joint disposal of tailings and waste rock. These field tests took place at the Minnamax copper- nickel exploration site near Babbitt (fig. 1).

---

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

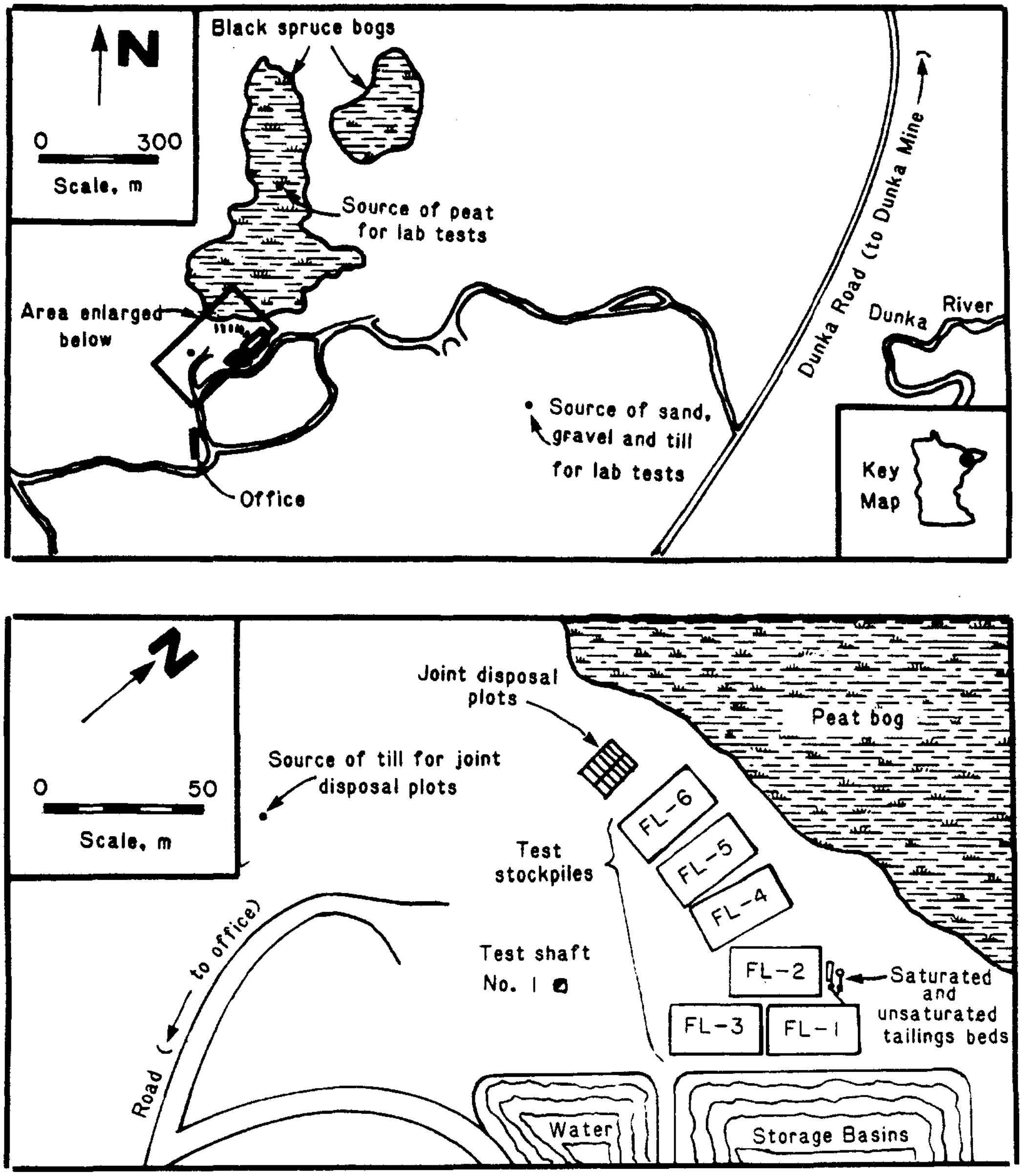


FIGURE 1.- Minnamax site, near Babbitt, Minnesota.

ACKNOWLEDGMENTS

The U.S. Bureau of Mines is gratefully acknowledged for the funding of this project, as is Peter Chamberlain for his cooperation and assistance. The authors also extend their sincere gratitude to the field staff of Dave Antonson, Anne Weir and Don Hendrickson and the laboratory staff of Jeanette Francetic, Al Klaysmat, Chuck Gruenenfelder, Susan Dullard and Annette Stiem. The authors appreciate all the efforts of those who contributed to the successful construction of the field experiments, with particular thanks to Eric Wolhome and Ed Holtan of the DNR Bureau of Engineering for design advice, Al Klaysmat and Bruce Johnson for construction supervision, the work crews of the Iron Range Resources and Rehabilitation Board for their labor in assembling the joint disposal bins, and the Erie Mining Company who donated personnel and equipment to load the tailings and waste rock into the joint disposal bins. The cooperation of AMAX, Inc., Kennecott Minerals Company, and INCO, Ltd. is also much appreciated. Thanks are also extended to Robert Young and his staff at the U. S. Department of Agriculture in Morris, to Iwao Iwasaki of the Mineral Resources Research Center, to Jeanete Leete of the DNR Division of Waters, and to Lisa Dahlgren of the DNR Division of Minerals for their specialized advice and assistance.

BACKGROUND

Metal sulfides are not thermodynamically stable in the presence of oxygen and water, and the sulfides oxidize to release trace metals and sulfate:

$$\mathrm{MeS(s) + 2O_2 = Me^{2+} + SO_4^{2-}} \qquad (1)$$

The release of iron from sulfide minerals leads to the formation of iron oxyhydroxide minerals (<u>91</u>, <u>121</u>) and the generation of acid:

$$\mathrm{2FeS(s) + 3H_2O + 9/2\ O_2 = FeO(OH)(s) + 4H^+ + 2SO_4^{2-}} \qquad (2)$$

The acid that is generated can be consumed by the dissolution of the silicate minerals present in the rock:

$$\mathrm{CaAl_2Si_2O_8(s) + 2H^+ + H_2O = Ca^{2+} + Al_2Si_2O_5(OH)_4(s)} \qquad (3)$$

The balance between the rates of acid generation and acid consumption determines the solution pH.

The transport of a components released from the mineral phase is controlled by the amount of water percolating through the stockpile, the composition of the percolating water (in particular pH), the chemistry of the released component, and the chemical character and surface area of solid surfaces present. The amount of percolating water is dependent upon the input volume and

subsequent flow routing. Precipitation is an everpresent input, but surface water and groundwater can also contribute under certain conditions.

Water input to a rock stockpile will be incorporated as storage or discharged as evapotranspiration, surface runoff, subsurface stormflow (or interflow) and baseflow (42, 56). Surface runoff can begin when the rate of precipitation exceeds the rate of infiltration. Subsurface stormflow is the peak subsurface flow response to a storm event. Baseflow is the long-term subsurface discharge that remains relatively unaffected by short-term storm events.

A number of low cost materials have been investigated for their ability to remove trace metals from solution. These materials include peat, bark, mineral soils, glacial materials, tailings, individual silicate minerals (including zeolite), lime and sponge iron. Previous research on the metal removal abilities of various materials is summarized below, and a more detailed discussion is presented in a separate volume (80).

The occurrence of elevated trace metal concentrations in peat has long been recognized by geologists (41, 83, 84) and has led to its use as a geochemical exploration tool (51, 85). Approximate geochemical enrichment factors (the ratio of the metal concentration in peat to the aqueous metal concentration) for Cu, Ni, Co, and Zn have been reported as 2,400, 450, 6,900, and 8,600, respectively (110). Copper concentrations of 2.2 to 8.9 pct of the dry peat mass have been reported (102, 115, 121) as have nickel and zinc concentrations of 2.3 and 3.3 pct, respectively (102, 121). The flow of gabbro stockpile drainage through a peat bog has produced Cu, Ni, and Co concentrations in peat ranging from 0.36 to 0.64 pct (30).

The trace metal removal capacity of peat can be positively correlated with both its pH (60) and cation exchange capacity (CEC). The CEC has been shown to increase with increasing organic matter content in peat (45). The majority of CECs from geographically widespread peat samples of varying compositions, however, were limited to between 100 and 200 meq/100 g (132).

The application of the metal sequestering properties of peat to waste water treatment was suggested as early as 1961 (95), and subsequent studies investigated the feasibility of its use for treating industrial (16, 19) and domestic wastes (14, 39). Peat from northeastern Minnesota was capable of removing metals from simple solutions containing only one metal (106) and from more complex solutions such as stockpile drainage (30, 31). Trace metals have also been removed by organic solids with compositions similar to peat, such as tree bark (104).

Mineral soils, tailings, and individual mineral fractions have also been examined for their ability to remove trace metals from solution. Batch and column studies indicated that mineral soils can remove trace metals from solution by adsorption (32, 40, 46, 47, 133) and precipitation (32, 40, 47). Several trace metals, including copper and zinc were "strongly attenuated" by calcium saturated clays and quartz sands in column tests (47). Flow through soil columns reduced copper concentrations to less than 0.03 mg/L and zinc concentrations to less than 0.2 mg/L from influent levels of 30 mg/L each (133). Glaciofluvial materials were also capable of reducing aqueous concentrations of heavy metals such as cadmium (40).

Tailings from a variety of mineral processing operations have been examined as a means of removing heavy metals from wastewater in several different studies. Broman (9) discussed the principles of metal removal by tailings due to both hydroxide precipitation and adsorption. Miller (86) also explained metal removal by tailings due to the same two mechanisms, and noted that the removal capacity was partly dependent on the mineralogy, particle size distribution and specific surface area of the tailings. This study reported maximum copper and zinc removal capacities of 12.6 and 17 mg/g, respectively. Beard, Salisbury, and Shirts (2) investigated the removal of radium and thorium from uranium mill processing waste waters in batch experiments with six soil and three tailings samples. As much as 97 pct radium removal 60 pct thorium removal was achieved.

Studies with individual silicate minerals commonly found in mineral soils, glacial materials and tailings have demonstrated significant capacities for trace metal removal. Capacities of 18.5 to 21.0 mg/g copper and 19.2 to 23.0 mg/g zinc were determined for montmorillonite and kaolinite in batch studies at pH 5 (47). Adsorption of these and other heavy metals increased with increasing pH and decreasing concentrations of competing ions (46, 47). The removal of trace metals by silicate minerals has been investigated in greater detail by several other researchers (9, 64, 65, 98, 133).

Zeolite minerals are naturally occurring cation exchangers which are capable of removing metals from waste waters (111, 112). The CECs determined for three types of clinoptilolite, one of the more commonly occurring zeolite minerals, ranged from 164 to 225 meq/100 g (112). Clinoptilolite was highly selective for Ba and Pb, but considerably less selective for Cu, Cd, and Zn, although these metals were preferred over Na (112). The extent of trace metal removal decreased with the presence of competing cations, such as Na, Ca, and Mg, decreasing pH and increasing flow rate (111).

Solids for treating stockpile drainage in a field setting could be contained in treatment beds external to the stockpile, or

mixed with the stockpiled rock. In a treatment bed hydrologic factors, as well as chemical factors, influence metal removal. The most important hydrologic variables are the distribution and residence time of flow within the bed (57, 76). The flow distribution will determine how efficiently the available metal removal capacity is used. If the majority of input passes through one region of the bed, the removal capacity of that region will be exhausted. No metals would be removed from additional flow, despite additional removal capacity in other regions of the bed.

Uniformity of flow depends principally on the shape and size of the bed particles, the means of inflow distribution, the size of the bed (both depth and plan area) and the rate of input (55, 101). Increased inflow in an unsaturated bed was found to result more in increased flow through existing flowpaths than in the creation of more flowpaths (3, 89). At lower inflows, however, the response to increased flow was mainly in more even flow distribution. Increased flow velocity tends to decrease removal, since there is less time for contact between the solids and solution and less time for metal diffusion (127).

Stockpile leachate quality is variable, and discharge is a function of snowmelt and precipitation, therefore, flow rates are variable. If stockpile leachate were directed to a treatment bed variable flow rates, particularly high flows, could reduce trace metal removal. Flow distribution could be uneven, since areas near the input could receive the majority of flow. This would reduce the utility of some of the solids in the bed, while the capacity of others was rapidly exceeded. These problems were among those which demanded attention in the field studies.

Three field studies were designed to investigate three different low cost, low maintenance techniques for mitigating trace metal release from stockpiles.These techniques were an unsaturated treatment bed, a saturated treatment bed, and the joint disposal of tailings and waste rock.

The objectives of the unsaturated bed study were to:

1) determine the trace metal mass removal by the bed;
2) determine the variation of effluent quality with
    a. input flow,
    b. cumulative flow volume,
    c. time,
    d. horizontal distance from input, and
    e. depth in bed;
3) determine the variation of output flow rate with
    a. input flow,
    b. cumulative flow volume,
    c. time, and
    d. horizontal distance from input; and
4) investigate field oriented problems which were not elucidated in the laboratory experiments.

The considerations for a saturated bed are similar to those for an unsaturated bed, with the exception of the question of flow distribution. In a saturated bed flow would be fairly evenly distributed among all particles in the bed, similar to the saturated columns in the lab phase. The objectives of the saturated bed study were to:

1) determine the trace metal mass removal by the bed and
2) determine the variation of effluent quality with
    a. cumulative flow volume,
    b. influent quality, and
    c. input flow.

The joint disposal of treatment solids and waste rock was directed at decreasing the oxidation of sulfide minerals and the amount of water percolating through the solids to transport trace metals and acid released by the oxidation. The objectives of this study were to:

1) determine the distribution of input precipitation among evapotranspiration, surface flow, interflow, and percolation through the pile;
2) examine the effects of vegetation on the magnitude of evapotransporation
3) examine the potential for adsorption of trace metals by the treatment solids; and
4) determine the influence of joint disposal on oxygen concentrations within stockpiles.

MATERIALS

Solids

Introduction

The materials chosen were readily available in northeastern Minnesota. Some modifications of the bulk samples, including removal of the fines, were required to increase the hydraulic conductivity of the solids and facilitate laboratory experiments.

Wood Chips

The wood chips were obtained from a sawmill near Embarrass, Minnesota. They were ground in a blender at high speed for one minute and then sieved to remove the less than 0.037 mm fraction. The ground wood chips were principally between 0.425 and 4.76 mm in size (table 1), with a low level of trace metals and sulfur compared to the other materials tested (table 2).

Peat

The fibric, woody peat was collected from the upper 0.75 m of a black spruce bog at the Minnamax site at a location uncontaminated by any mining activity (fig. 1). The pH and CEC

TABLE 1. - Particle Size Distribution of Solids

(Analyses by Physical Testing and Inspections Laboratory, Minnesota Department of Transportation, St. Paul)

Particle diameter, mm	Pct finer than									
	Laboratory Tests						Field Tests			
	Batch				Column		Tailings treatment bed[1]	Joint disposal plots		
	Wood Chips	Till	Tailings	Clinoptilolite	Till	Tailings		Gabbro material	Till	Tailings
Boulders and cobbles										
305	100	NA	NA	NA	100	NA	100	89.0	NA	NA
152	100	NA	NA	NA	100	NA	100	82.2	NA	NA
Gravel										
76.2	100	NA	NA	NA	100	NA	100	67.7	NA	NA
50.8	100	98.3	NA	NA	100	NA	100	NA	NA	NA
25.4	100	95.8	NA	NA	100	NA	100	38.3	NA	NA
19.0	99.5	91.6	NA	NA	100	NA	100	33.8	NA	NA
15.9	99.4	NA	NA	NA	100	NA	100	NA	NA	NA
12.7	99.3	NA	NA	NA	100	NA	100	27.1	NA	NA
9.4	98.8	84.1	NA	NA	100	NA	100	NA	99.5	NA
6.4	NA	NA	NA	NA	100	NA	100	19.2	NA	NA
4.76	95.9	78.4	NA	NA	100	NA	100	NA	96.2	NA
Sand										
2.00	68.5	66.4	99.2	99.4	84.6	98.7	100	12.2	86.4	[1]97
1.41	NA	NA	NA	NA	NA	NA	NA	10.8	NA	NA
0.84	19.1	52.9	98.9	98.5	67.5	98.2	[1]99.9	10.6	72.9	NA
.425	4.0	37.5	98.6	7.1	48.0	97.7	[1]99.1	7.7	60.9	[1]97
.250	NA	27.1	94.6	4.8	34.7	91.0	[1]90.3	6.1	50.6	NA
.177	NA	NA	NA	NA	NA	NA	[1]72.1	NA	NA	NA
.149	0.2	17.4	77.0	3.7	22.3	59.3	[1]62.0	4.6	40.0	[1]95
.105	NA	NA	NA	NA	NA	NA	35.0	3.4	NA	[1]92
Silt										
.075	.1	8.1	41.1	2.6	10.4	0	[1]25.5	3.1	29.4	[1]83.5
.037	0	0	0	0	0	0	NA	NA	NA	NA
Clay										
.002	0	0	0	0	0	0	6.5	NA	4.8	[2]5.9

NA = Not available

[1] Mean of two or more analyses.

[2] A 36.3 pct clay value was also obtained, but was considered erroneous because it was so far from the 4.5 and 2 pct clay values obtained by the West Central Experiment Station of the University of Minnesota at Morris; the 5.9 pct value as well as the values for other size fractions were close to those obtained by the West Central Experiment Station.

NOTE.-Boulders, cobbles, gravel, sand, silt and clay refer to U.S. Department of Agriculture (USDA) soil classification definitions.

TABLE 2.- Chemical Characterization of Solids

(Data reported on less than 2 mm diameter size fraction on an air-dry basis, unless noted)

Material	Pct carbon	pH (whole sample)	CEC, meq/100 g	Exchangeable cations, meq/100g				Bray-1 phosphorus, mg/kg	Pct nitrogen	Total element content, mg/kg				
				Na	K	Ca	Mg			S	Cu	Ni	Co	Zn
Laboratory														
Batch														
Wood chips...	[1]53.4	4.65	15.38	<0.11	<0.70	2.76	1.03	NA	NA	[1, 2] 270	[1, 2]8.0	[1, 2]2.0	NA	[1, 2]19.4
Peat.........	[1]53.6	4.46	105.13	.40	.53	20.54	11.39	NA	NA	[1, 3]1,760	[1, 3]5.7	[1, 3]4.2	NA	[1, 3]10.2
Till.........	0.81	5.25	10.6	.03	.12	2.73	1.07	NA	NA	200	140	140	90	80
Tailings.....	.10	7.27	4.08	.10	.06	3.28	0.64	NA	NA	950	360	460	120	150
Zeolite......	.28	7.80	149.31	92.48	43.95	11.54	1.34	NA	NA	300	60	40	30	30
Column..........														
Peat.........	[1]53.6	4.46	105.13	.40	.53	20.54	11.39	NA	NA	[1, 3]1,760	[1, 3]5.7	[1, 3]4.2	NA	[1, 3]10.2
Till.........	.93	5.31	7.87	.04	.08	2.28	.84	NA	NA	200	150	160	80	90
Tailings.....	.08	7.36	4.05	.10	.02	3.23	.70	NA	NA	950	390	430	110	130
Field..............														
Tailings treatment beds.....	.028	6.36	1.83	.07	.07	1.08	.61	1.5	0.001	1,350	470	470	130	120
Joint disposal..														
plots.........														
Till.......	.81	5.78	10.65	.03	<.02	1.12	.62	19	.046	200	180	150	80	80
Tailings...	.56	6.87	6.96	.31	.09	5.45	1.11	5	.006	3,800	420	350	110	180

NA Not available.

[1] Sample dried for 24 to 48 hours at 65 to 75° C.

[2] Analysis was on ash, which was 1.15 pct mass of dried sample.

[3] Analysis was on ash, which was 8.53 pct mass of dried sample.

were toward the lower end of the range for northern Minnesota peat, while the trace metal content was in the upper end of that range (5, 48). The saturated water content of the peat, on a wet volume basis, was 89.5 pct, which is typical for peats (4).

In column experiments peat was mixed with sand, in a 2:1 mass ratio of wet peat:sand, since previous experiments indicated that peat alone transmitted flow too slowly to be practical in column tests. The sand peat mixture had a saturated hydraulic conductivity of 5.4 x 10^{-4} cm/s, when packed at a dry bulk density of 1.2 g/cm^3 in a falling head permeameter test. The peat-sand mixture in the columns had a dry bulk density of 1.0 to 1.2 g/cm^3 and a porosity of 0.4 to 0.5.

Glacial Materials

The till for the laboratory experiments and for the joint disposal plots was a loamy sand material collected at two separate sites on the Minnamax property (fig. 1). This material was Rainy Lobe till, the major surficial deposit in the copper-nickel resource area (117). The joint disposal till had a particle size distribution (table 1) that was typical of till in the region of proposed copper-nickel mining (69, 93, 99, 103). The gravel, finer silt and clay fractions were removed from the till for laboratory use. In the sand fraction of till from the Filson Creek area which has bedrock geology similar to that of the Minnamax site, plagioclase was by far the most common mineral, with lesser amounts of quartz, biotite, microcline, hornblende, pyroxenes, olivine and opaque minerals (113). The clay fraction was dominated by quartz, kaolinite, chlorite and feldspars.

The chemistry of the till samples was only in part representative of Rainy Lobe deposits in northeastern Minnesota. Sample pH values (table 2) and nitrogen and phosphorus levels were similar to those reported for several till samples in the area (69, 99, 103). Carbon and CEC levels were closer to those concentrations reported for till from upper soil horizons rather than till sampled at depth (69, 99). This seems to indicate that the samples included a considerable amount of surface material in which soil development had occurred. Trace metal levels in the samples were much higher than those reported in Rainy Lobe till sampled about 40 km south of the Minnamax site (99). The former till had Cu and Ni levels about three times as high as the latter till, while Zn levels were elevated to a lesser extent. Moisture retention data for the joint disposal till are presented in table 3 and the saturated hydraulic conductivities measured for the till samples appear in table 4.

The sand and gravel used to pack the ends of the columns in the laboratory experiments were also obtained at the Minnamax site (fig. 1). No chemical or mineralogical analyses were performed on this material, which appeared to be mostly quartz and feldspar.

TABLE 3.—Moisture Retention Data for Till and Tailings

(Values expressed on a wet mass basis)

Sample	Moisture content, pct					
	-0.05 bars	-0.1 bars	-0.33 bars	-1 bars	-5 bars	-15 bars
Joint disposal till[1]...	NA	17.5	13.4	NA	NA	5.5
Joint disposal tailings...........	NA	29.0	NA	NA	NA	1.4
Treatment bed tailings[2]..........	11.1	7.0	3.5	1.8	1.0	0.8

NA Not available.

[1] Mean of two samples.

[2] Packed bulk density of 1.70 g/cm^3; bulk density was not measured for other samples.

TABLE 4.-Saturated Hydraulic Conductivity of Till and Tailings

Sample	Packed bulk density, g/cm^3	Estimated porosity[1], pct	Hydraulic conductivity, cm/s
Batch till..........	1.18	55	1.33×10^{-2}
Joint disposal till.	1.33	50	1.86×10^{-4}
Joint disposal till.	2.13	20	8.34×10^{-7}
Batch tailings......	1.85	37	1.19×10^{-4}
Treatment bed tailings[2]........	1.6	46	8.8×10^{-4}
Treatment bed tailings.........	1.7	42	5.4×10^{-4}
Treatment bed tailings[3]........	1.86	37	2.2×10^{-4}
Joint disposal tailings.........	1.55	47	1.6×10^{-4}
Joint disposal tailings.........	1.85	37	4.71×10^{-5}

[1] Material densities of 2.65 g/cm^3 for till and 2.94 g/cm^3 for tailings were assumed.

[2] Mean of four analyses.

[3] Mean of two analyses.

TABLE 5.-Specific Surface Area of Tailings

(Mean of two values)

Sample	Specific surface area, m^2/g
Batch.............	1.3
Column............	0.80
Treatment bed........	.68
Joint disposal........	1.6

Tailings

The three different low sulfide tailings samples used had rather different source histories. Different samples were used due to depletion of the initial supplies. Each is briefly described below, and Duluth Gabbro processing in general is discussed by Veith (129).

The tailings used in the laboratory experiments were processed by Lakefield Laboratories of Lakefield, Ontario, from ore produced from Minnamax test shaft number one (fig. 1). A selective flotation process was employed, using three stages of copper-cleaner flotation and three to four stages of copper-nickel-cleaner flotation. Chemical additives during the processing included: dithiophosphate, potassium amyl xanthate and sodium isopropyl xanthate as collectors; SO_2 and lime as nickel depressants; $CuSO_4$ as a pyrrhotite activator; and methyl isobutyl carbinol (MIBC) as a frother. The less than 0.037 mm and less than 0.075 mm fractions were removed from the batch and column tailings, respectively, before use, in order to provide a defined surface area for the calculation of removal capacities and to achieve a sufficiently high hydraulic conductivity for adequate column flow.

The treatment bed tailings were generated by INCO, Ltd., at their Creighton Mill in Ontario, from ore produced from their Spruce Road site near Ely, Minnesota. The bulk flotation process used included the typical rougher, cleaner and, scavenger flotation stages. Potassium amyl xanthate and MIBC were added to the flotation circuit, as a collector and a frother, respectively. The tailings generated were placed in the tailings basin at Copper Cliff, Ontario, fertilized with 5-20-20 fertilizer at a rate of 340 to 780 kg/ha, and vegetated. The tailings remained in this basin for about seven years, after which they were excavated and shipped to Minnesota for the study.

The joint disposal tailings were processed by the Twin Cities Research Center of the U.S. Bureau of Mines (109) from ore obtained from Minnamax shaft number one (fig. 1). A bulk flotation process was used similar to that employed by INCO. Sodium isopropyl xanthate and MIBC were added to the flotation circuit, as a collector and a frother, respectively.

The tailings used in the joint disposal plots could be labeled a silty loam, and were finer than the other tailings samples (table 1). The treatment bed, batch and column tailings, respectively, had loamy sand, sandy loam and fine sand textures. The specific surface areas of the batch and joint disposal tailings were about twice that of the column and treatment bed tailings (table 5). The particle size distribution of the treatment bed tailings appears to be closest to that expected from a full-scale ore processing operation (61, 24).

The chemical properties of the different sets of tailings also varied, although the batch and column tailings were generally similar (table 2). The chemical properties of the tailings samples were generally similar to those measured for other copper-nickel tailings produced from the Duluth Complex (8, 61, 63, 94, 109, 124), although trace metal contents were somewhat higher than those reported by Borovsky (8).

The mineralogy of the tailings was not analyzed, but it could be expected to be similar to that of the initial ore. This ore was approximately 40 to 70 pct plagioclase, with about 15 to 40 pct combined olivine, pyroxene and amphibole (117). Chlorite, biotite and smectite have each been found in ore at levels less than 5 pct (117). Some of the sulfur and trace metals in the gabbro do not occur as discrete metal sulfides, but are included within olivine, pyroxene and plagioclase (61). Previous exposure of the samples to weathering processes, as occurred with the treatment bed tailings at Copper Cliff, might have lead to the formation of smectite, kaolinite or jarosite (105).

The moisture retention of the joint disposal tailings was considerably higher than the treatment bed tailings (table 3). Saturated hydraulic conductivity values obtained for the tailings samples varied just over an order of magnitude, between 8.8×10^{-4} and 4.71×10^{-5} cm/s (table 4). There was little difference in conductivity among the three sets of tailings tested; the conductivity of the column tailings might be expected to have been greater due to the removal of fines. Conductivity decreased with denser packing, but by less than an order of magnitude.

Zeolite, Lime and Sponge Iron

The clinoptilolite sample was obtained from the Anaconda Company as Zeolite 1010A[5], and was from the same material used by Semmens and Martin (111) in their study of the removal of Pb, Cd and Ag from saline waters. In contrast to the sample used by Semmens and Martin (111), however, the DNR sample was not conditioned prior to use. The fraction finer than 0.037 mm diameter was removed, and the material had a coarse sand texture (table 1).

The lime and sponge iron were tested only in the preliminary batch experiments, and thus were not characterized as were the other five solids. The lime was obtained from the Western Lime Company of Blaine, Minnesota, under the trade name Miracle Lime. The sponge iron was provided in 1980 by Dr. Iwao Iwasaki of the Mineral Resources Research Center (MRRC), and was representative of commercially available sponge iron.

---

[5] Reference to specific products does not imply endorsement by the Bureau of Mines.

Gabbro Material

The gabbro material used to construct the joint disposal plots was obtained from test stockpile FL-4 at the Minnamax site (fig. 1). This was one of six test stockpiles constructed in 1977 to study stockpile leaching and various mitigation techniques (29).

The particle size distribution of the gabbro material is presented in table 1. Only the sand, silt and clay fractions were analyzed for specific surface area, chemistry and mineralogy. The specific surface area of the fine fractions was roughly inversely proportional to the particle diameter, but higher than was estimated assuming smooth spherical, nonporous particles (77). The pH decreased and the sulfide and trace metal content increased with decreasing particle size of the gabbro material (table 6). X-ray diffraction (XRD) analyses were conducted on the 0.053 to 0.075 mm, the 0.075 to 0.0105 mm, and the 0.0105 to 0.149 mm size fractions of the gabbro material. Approximately half of this material was plagioclase (with a Na:Ca ratio of about 2:3), and half was a mixture of olivine (with a Fe:Mg ratio of 1:4 to 1:9), pyroxene, and biotite. Lesser amounts of magnetite, amphibole, chlorite and possibly smectite and/or vermiculite were also identified. The phyllosilicate minerals (biotite, chlorite, smectite, and vermiculite) were more common in the finer size fractions.

Leachate Solutions

The mine stockpile drainage used in the laboratory and in the tailings treatment beds was collected from three sources: Dunka Mine monitoring site EM-8 and Minnamax test stockpiles FL-1 and FL-5 (fig. 1). The composition of these three solutions varied with time. The EM-8 site was located about 300 m downsteam of seepage from a 15 million metric ton (Mmt) wasterock stockpile composed of sulfide-bearing gabbro, which averaged 0.057 pct Cu and 0.014 pct Ni (56). Test stockpiles FL-1 and FL-5 were two of six 800 to 1,300 mt plots constructed in 1977 to study leachate generation and control (29). The sulfide-bearing gabbro in pile FL-1 (0.63 pct S, 0.35 pct Cu, 0.083 pct Ni) was obtained from test shaft number 1 (fig. 1), while the gabbro in pile FL-5 (1.41 pct S, 0.30 pct Cu, 0.085 pct Ni) was excavated from an underground drift. The physical characteristics of the stockpile material were similar to those of the FL-4 material previously described. The chemistry and mineralogy of stockpile FL-1 were also probably close to those of FL-4; the FL-5 material varied from that of FL-4 due principally to its higher metal sulfide content.

The leachate solutions used were chosen to represent a range of compositions, and were based on water quality source models for a copper-nickel mining operation (123). The four trace

TABLE 6. - Characterization of Fine Fractions, Joint Disposal Bin Gabbro Material

Size fraction, mm	pH	Chemical content, pct						Specific surface area, m^2
		S		Cu	Ni	Co	Zn	
		Total	Sulfide					
Sand								
0.50-2.00....	6.56	0.67	0.65	0.337	0.062	0.012	0.015	0.60
.177-0.50...	6.37	.80	.75	.381	.078	.013	.015	.78
.149-.177...	6.18	.88	.80	.391	.103	.015	.015	1.1
.105-.149...	NA	1.12	1.05	.495	.147	.019	.017	1.6
.074-.105...	5.95	1.37	1.30	.585	.221	.022	.019	1.7
Silt and clay								
.053-.074...	5.78	1.65	1.57	.647	.253	.024	.019	2.6
<.053.......	5.77	1.94	1.86	.814	.295	.027	.023	4.7

NA Not available.

Particle size distribution presented in table 1.

metals, Cu, Ni, Co, and Zn, would be those most likely to cause adverse impacts, according to source models and toxicity data. Johnson and Lieberman (67) normalized the toxic effects of these four metals by defining the copper equivalent unit (CEU):

$$[\mathrm{Cu}] + 0.1\,[\mathrm{Ni}] + [\mathrm{Co}] + 0.1\,[\mathrm{Zn}] = \mathrm{CEU}, \qquad (4)$$

where [ ] represents aqueous concentration in mg/L. The CEU essentially converts the toxic effects of all trace metals into those that would be expected for a copper concentration equal to the CEU value. It assumes that the various metal toxicities are additive.

Three solutions, designated Leachates A, B and C, were used in the laboratory studies. Leachates A and C were collected from FL-1 and FL-5 runoff, respectively, between September 1980 and July 1981. Leachate B consisted of EM-8 water collected between September 1980 and September 1981 that was occasionally spiked with Ni, Co and Zn standards to maintain a rather constant composition. Of the three leachate solutions tested, Leachate C had by far the lowest pH and highest trace metal concentrations. The other two leachate solutions, in contrast, had pH values in the near neutral range, and much lower trace metal levels (table 7). Of these two solutions, Leachate B generally had higher pH values, and trace metal concentrations.

LABORATORY EXPERIMENTS

Batch

Methods

The batch experiment apparatus consisted of parafilm covered 250-mL Erlenmeyer flasks that were agitated on an Eberbach rotating shaker. A leachate volume of 100 mL was used in the flasks. Preliminary batch studies were conducted on wood chips, peat, till, tailings, zeolite and lime with leachates A, B and C. These tests were used to determine the mass loading ranges for most effective trace metal removal and the time required for removal reactions to reach equilibrium. Mass loading ranges from 1 to 100 g/L and a reaction time of 7 days were selected for subsequent tests at controlled pH levels with Leachates A and B. Virtually all samples in these batch tests and the subsequent column and field tests were filtered through a 0.45 um filter to remove particulates.

In the controlled pH experiments, seven to nine different mass loadings were run at pH 7.4. Three additional pH values were examined for each solid at three different mass loadings. The pH range chosen was based on the solution pH that had been produced in the preliminary experiments. For wood chips, peat, and till a pH range of 4 to 7.4 was used, while for tailings and zeolite a pH

TABLE 7. - Composition of Leachate Solutions Used in Laboratory Tests

Solution	pH	Concentration, mg/l							Concentration, mg/L as $CaCO_3$		Specific Conductance, uS/cm
		Filtered Cu	Filtered Ni	Filtered Co	Filtered Zn	Filtered CEU	TOC	DO	Total Alkalinity	Hardness (Ca, Mg)	
Leachate A											
Mass loading batch test.	7.37	0.038	0.80	0.040	0.10	0.168	NA	NA	NA	1,140	2,300
Kinetics batch test.	6.88	.02	.86	.04	.08	.15	NA	NA	NA	NA	2,500
Isotherm batch test.	7.40	.046	1.06	.029	.11	.195	NA	NA	NA	1,430	NA
Column test..	7.20-7.43	.02-.04	.78-1.08	.05-.06	.03-.12	.16-.22	10	8.4	24	600-790	NA
Leachate B											
Mass loading batch test.	7.86	.13	8.38	.28	.18	1.26	NA	NA	NA	1,430	2,500
Kinetics batch test.	7.67	.10	7.75	.24	.20	1.14	NA	NA	NA	NA	2,400
Isotherm batch test.	7.40	.08	8.62	.33	.22	1.29	NA	NA	NA	1,330	NA
Column test..	7.22-7.87	.01-.06	4.70-5.99	.14-.25	.05-.23	.64-.85	22	7.8	69	804-1,480	NA
Leachate C											
Mass loading batch test.	3.23	111.3	424	26.4	15.6	181.7	NA	NA	NA	3,070	>5,000
Kinetics batch test.	3.10	126	418	27.4	16.0	197	NA	NA	NA	NA	8,000

NA Not available.
NOTE. - All analyses corrected to 25° C.

range of 6 to 8 was examined. 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, in the case of peat, bog water (table 8). The rinse solutions were maintained at the same pH as were the leachate solutions in the removal phase.

Results

Preliminary Experiments

The preliminary batch studies indicated that the solids were capable of reducing CEU levels by as much as 90 pct and that peat, wood chips, and till tended to reduce solution pH. Kinetic studies indicated that the majority of trace metal removal occurred within the first 20 h and that most reactors reached equilibrium after approximately 70 h of reaction.

In the preliminary experiments lime and sponge iron were the only solids effective in removing metals from Leachate C, which had initial CEU and pH values of 181 mg/L and 3.2, respectively. The lime was used for comparative purposes, since it is the most widely used material for neutralizing acid mine drainage (52). The percent CEU reduction at the maximum loading of 50 g/L decreased in the order lime (100 pct at 20 g/L), wood chips (82 pct), zeolite (68 pct), peat (62 pct), till (32 pct),and tailings (16 pct). Equilibrium pH values for the solids decreased in the order lime (8.1), zeolite (5.2), tailings (4.3), till (3.8), wood chips (3.3), and peat (2.9). The trace metal removal by sponge iron at 20 g/L was greater than that by the other solids at all loadings. The sponge iron also elevated solution pH. At a sponge iron mass loading of 50 g/L, CEU levels were reduced from the initial level of 181 mg/L to 4.5 mg/L, and pH was elevated from 3.2 to 4.7.

Trace Metal Removal in Batch Solutions at pH 7.4

The effectiveness of solids in reducing CEU levels of Leachate A decreased in the order peat, zeolite, till, tailings, wood chips (fig. 2). The performance of peat is actually underestimated in fig. 2 since its removal is expressed in terms of the wet mass of peat, while dry mass is used for the other solids. The dry mass of peat is approximately one-tenth of the wet mass. Thus, for peat, the mass loading of 50 g/L (fig. 2) is actually 5 g/L, and so on. The maximum CEU removal by the various solids ranged from 45 to 80 pct, and was largely due to the removal of nickel, which constituted more than 70 pct of the initial 0.195 mg/L CEU level. The variation in equilibrium concentrations of Cu, Co and Zn over the loading range for a given solid was typically less than a factor of two. The effectiveness of the solids in removing copper followed approximately the same order as for CEU reduction. Typical equilibrium concentration ranges for cobalt and zinc were 0.02 to 0.06 mg/L for all solids except wood chips, which produced elevated zinc concentrations.

TABLE 8. - Composition of Rinse Solutions Used in Batch Tests

Solution	pH	Concentration, mg/L								
		Filtered metals					Ca	Mg	Na	K
		Cu	Ni	Co	Zn	CEU				
Distilled water...	4.0,7.4	<0.001	0.002	0.001	0.003	0.002	<0.01	<0.01	<0.01	<0.01
Salt solution.....	7.4	<.001	.018	.003	<.001	.005	395	38.9	127	37
Bog water.........	3.97	<.001	.004	.002	.008	.003	3.8	3.0	1.1	1.3

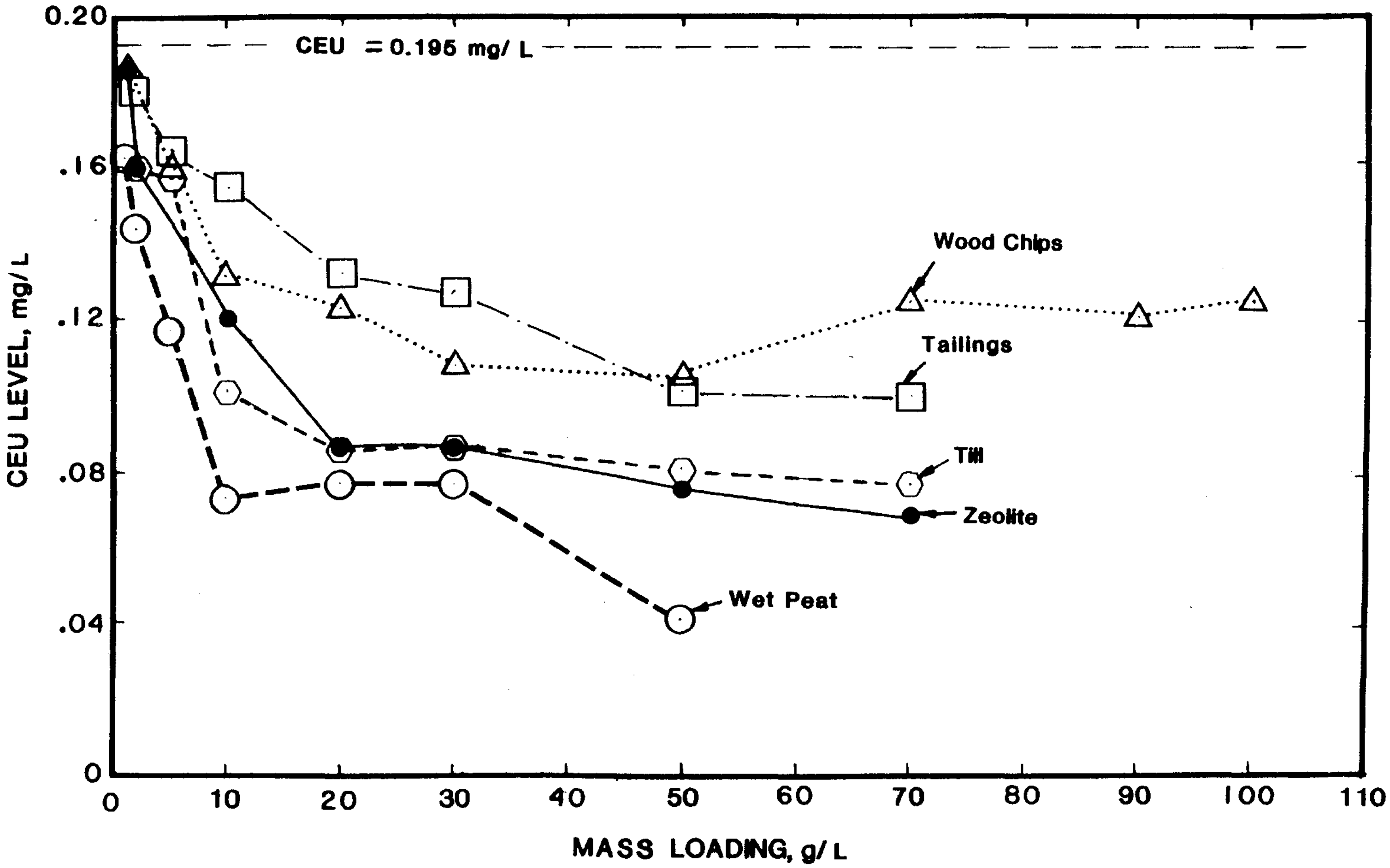


FIGURE 2.- Isotherm batch experiment with Leachate A at pH 7.4: CEU level versus mass loading.

The effectiveness of the solids in removing trace metals from Leachate B (decreasing in the order peat, till, tailings, zeolite, wood chips) was similar to that for Leachate A, with the exception of zeolite (fig. 3). Maximum observed CEU reductions ranged from 52 pct for wood chips to 92 pct for peat. The reductions were largely a function of nickel and cobalt removal.

Effect of Batch Solution pH on Trace Metal Removal

Trace metal removal decreased with decreasing pH. This relationship was quantified using linear regression, and the constants determined are presented in table 9.

Trace Metal Release in Batch Solutions

The rinse phase was designed to determine if the metals were strongly attenuated by the solids, or if they would be released to the environment when contacted by a given solution. Each of the solids used in the removal experiments at pH 7.4 was placed in contact with 100 mL of distilled deionized water which was maintained at pH 7.4. The solids which were more effective in removing metals from solution also retained metals more effectively in these rinse tests. Release of trace metals from peat and till used in experiments with Leachate A generally produced CEU levels less than 0.01 mg/L, while release from wood chips, tailings and zeolite typically produced levels in the range of 0.01 to 0.02 mg/L. The solids used in removal experiments with Leachate B typically produced CEU concentrations less than 0.06 mg/L. Trace metal release from peat was less than that from other solids, and release from till and tailings was generally less than that from wood chips. Release from zeolite was usually greater than that from the other solids, producing maximum CEU levels of 0.16 mg/L (fig. 4).

At pH 7.4 a net CEU removal occurred with most solids at most mass loadings. Net metal removal increased as loading increased except with wood chips, which released metals at higher loadings. In general, net CEU removal decreased in the order peat, till, tailings, zeolite, and wood chips. The maximum net removals per unit mass were typically observed at the lowest mass loadings. The maximum CEU removal capacities of peat, wood chips, tailings, till, and zeolite from Leachate A were 270, 210, 3, 37, and 8 mg/kg dry solid. The corresponding values for Leachate B were 3,400, 1,800, 680, 230, and 50 mg/kg dry solid.

The release of trace metals from the peat, wood chips, and zeolite used in removal experiments with Leachate A was relatively constant with respect to pH. Release from tailings and till tended to increase with decreasing pH and increasing loading. Release from all solids used with Leachate B tended to increase with decreasing pH. This trend was more pronounced for peat, wood

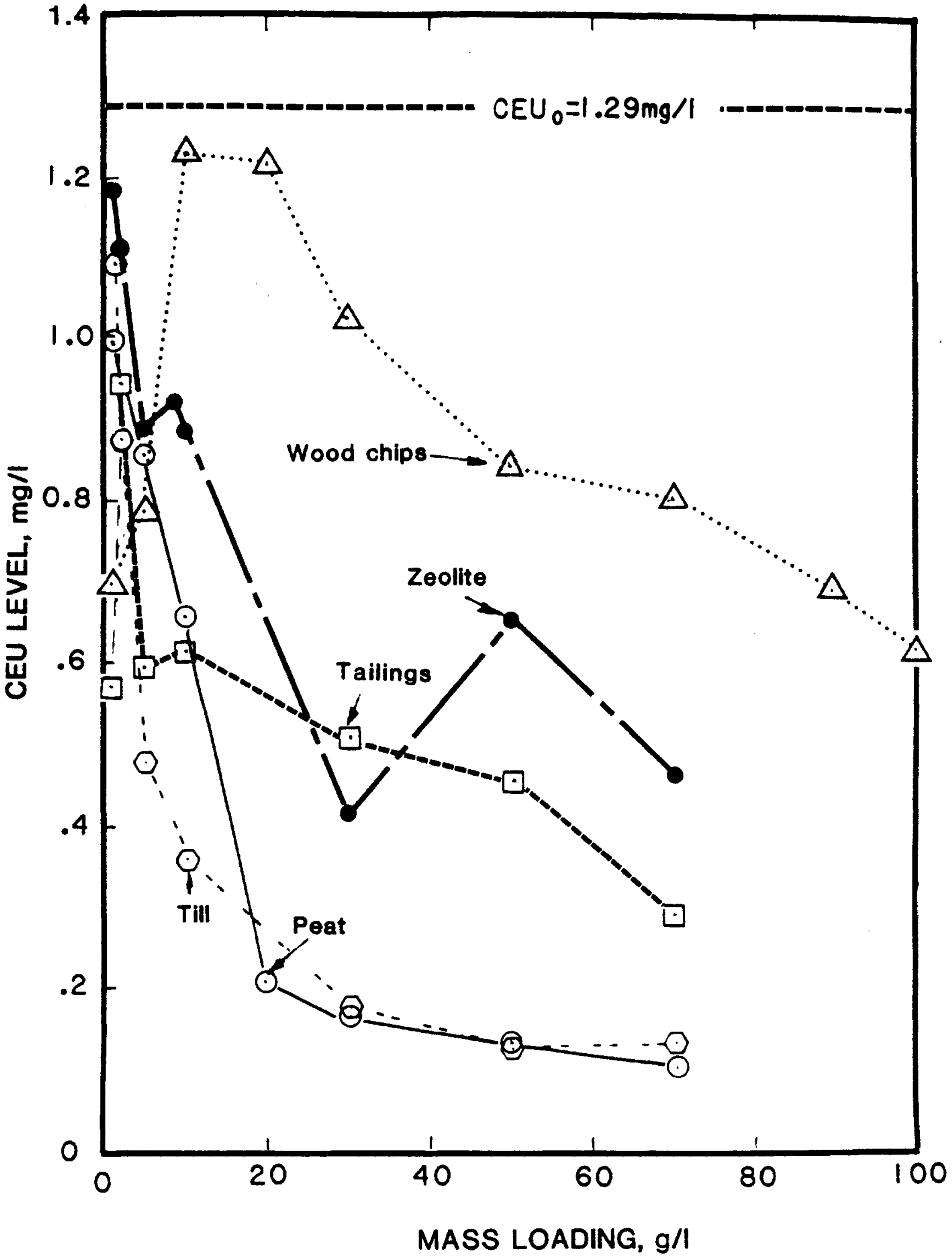


FIGURE 3.- Isotherm batch experiment with Leachate B at pH 7.4: CEU level versus mass loading.

TABLE 9. - Linear regression constants for equilibrium CEU levels as a function of pH

(Equilibrium CEU level in mg/L)

		Leachate A				Leachate B			
Solid	Experimental pH values	Mass loading, g/l	$\log(CEU_e) = a(pH) + b$			Mass loading, g/l	$\log(CEU_e) = a(pH) + b$		
			a	b	r^2		a	b	r^2
Peat[1]	4,5,6,7.4	1	-0.038	-0.532	0.74	1	-0.047	0.38	0.64
		10	-.13	-.127	.98	20	-.19	.66	.59
		50	-.17	-.150	.95	70	-.28	1.11	.98
Wood Chips	4,5,6,7.4	1	-.010	-.643	.43	1	-0.12	.68	.87
		20	-.084	-.266	.96	20	-.022	.26	.85
		70	-.10	-.168	.98	70	-.073	.45	.99
Tailings	6,7,7.4,8	2	-.080	-.183	.47	1	-.066	.50	.95
		20	-.25	.969	.93	10	-.23	1.53	.93
		70	-.58	3.39	.81	70	-.51	3.26	.95
Till	4,5,6,7.4	1	-.037	-.508	.90	1	-0.37	.35	.53
		20	-.15	.037	.98	10	-.19	1.08	.81
		70	-.18	.25	1.00	70	-.35	1.82	.95
Zeolite	6,7,7.4,8	1	-.015	-.595	.43	1	-.070	.54	.54
		20	-.13	-.146	.95	10	-.33	2.23	.77
		70	-.070	-.637	.85	70	-.056	.063	.089

[1] Wet mass was used for peat; dry mass approximately equals 0.1 X wet mass.

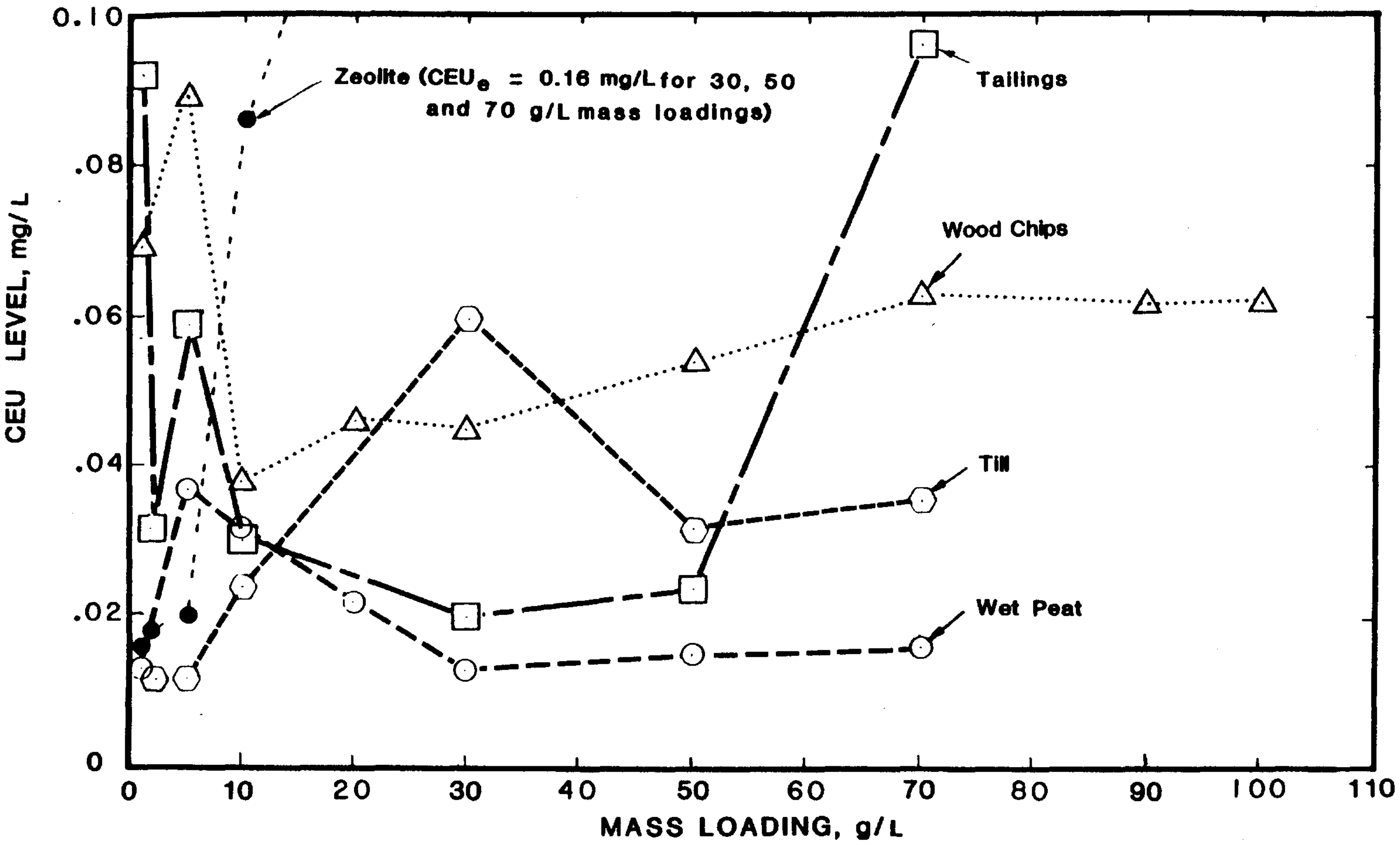


FIGURE 4.- Isotherm rinse batch experiment with Leachate B at pH 7.4: CEU level versus mass loading.

chips, and till, solids examined over the pH range of 4 to 7.4. The net CEU removal for these solids was typically negative at pH 4, indicating a release of trace metals, and increased with increasing pH. Tailings and zeolite were examined over the pH range of 6 to 8, with tailings exhibiting a net CEU release at pH 6. The net trace metal removal by both solids increased with increasing pH.

In addition to distilled deionized water, metal release to a salt solution (pH 7.4) and to bog water (pH 3.97) was examined. Samples of each solid were run with the salt solution. The most pronounced difference between the salt solution and distilled deionized water at pH 7.4 was an increase in the equilibrium CEU levels for the Leachate B peat and wood chips. The bog water rinse was used only with peat and produced equilibrium CEU values five to ten times higher than those observed for distilled deionized water at pH 4.0.

Discussion

Batch experiments provided certain benefits which would have been difficult to obtain in column experiments. Batch experiments were run in less time than column experiments and, therefore, provided an effective format for screening solids. The influence of the individual solids on trace metal concentrations and solution pH was readily surveyed in these experiments. In addition to comparing the various solids, the behavior of individual trace metals was also compared. The shorter time frame plus the control over reaction conditions allowed investigation of specific variables, in particular, the effects of mass loading, reaction time, and pH. Batch tests also examined metal release from the solids and the influence of pH, ionic strength, and for peat only, bog water, on trace metal release.

The preliminary batch tests, aside from helping to determine appropriate mass loading and reaction times for subsequent tests, demonstrated the limited success of the low cost materials in removing trace metals from Leachate C (pH less than 3.3, metal concentrations of 15 to 500 mg/L). Leachate C represents mine drainage that is highly contaminated both from the standpoint of acidity and trace metal levels, which were two to three orders of magnitude above U. S. Environmental Protection Agency (EPA) guideline limitations (126). Further experiments with Leachate C were conducted using sponge iron, which is capable of removing trace metals from concentrated leachates (62). The experiments indicated the use of sponge iron might be an economically viable recovery method. Based on the market values of the four metals in 1983 (33), $250 to $300 worth of metals per ton of sponge iron was recovered at a mass loading of 10 g/L. Nickel provided a higher market value recovery than did copper, cobalt or zinc (79).

In the batch tests with Leachates A and B, the relatively high level of nickel removal was most likely due to the correspondingly high nickel concentrations in the initial solutions. The more constant equilibrium concentrations of Cu, Co and Zn over the range of mass loadings indicated that the leachate concentrations for these metals neared the equilibrium level for the leachate-solid systems. These three metals may have been present largely as complexes that were not conducive to removal (20). The apparent cobalt release in the Leachate A experiment at constant pH, was not observed in the preliminary tests, and may be due to an erroneous value for initial cobalt concentration.

Although the data from the controlled pH tests were qualitatively useful metal removal capacities for the solids could not be quantified using Langmuir theory, which is often applied to adsorption data. Experimental data correlated well with the Langmuir isotherm equation, but most of the theoretical capacities predicted by this method were negative, and thus in disagreement with observed trace metal removal. This inconsistency is not unreasonable, since this application of Langmuir theory assumes that removal is the result of adsorption by a homogeneous surface from a simple solution (135). The presence of more than one type of metal ion susceptible to sorption may have complicated isotherm analysis (75). It is also likely that other mechanisms, such as ion exchange (32, 40, 46, 133) and complexation (18, 115), were also involved in removal reactions. Even though removal capacities were not obtained, the isotherm equation was useful in providing a fairly accurate description of the observed results.

Reactions with solid surfaces, either organic or inorganic, were undoubtedly responsible for the majority of metal removal by the low cost solids. These solids would be comparable to soils, where most trace metal adsorption appears to occur on organic matter, layered silicate clay minerals, and iron and manganese oxides, hydroxides and oxyhydroxides (98). Organic surfaces can bind metals by physical adsorption (10, 11, 12), chemisorption (34, 35, 36, 97), complexation (18, 115) or chelation (21, 22, 73, 74, 115). Wood chips and peat are almost completely organic, and till typically contains a small organic fraction. The tailings, however, had very little organic matter, consisting instead of largely plagioclase, pyroxene and olivine minerals. These minerals have rather low adsorptive capacities, indicating that lesser amounts of layered silicates and/or iron oxides and hydroxides could have accounted for a large part of the trace metal sorption.

Trace metal removal increased with increasing pH for all materials tested. This trend was consistent with previously reported research (9, 46, 60, 64, 65, 131). Based on the batch results tailings, till and peat were chosen for further study in the columns. Wood chips were eliminated because of their

relatively poor performance in removing and retaining trace metals at pH 7.4. Zeolite and lime were discarded due to their relatively high cost in a full-scale treatment scheme.

Column

Methods

The solids tested were packed into acrylic columns that were 91 cm long with an inside diameter of 2.54 cm (fig. 5). Layers of graded, acid washed gravel were placed above and below the treatment bed, and the solids were supported by a Swinnex Millipore filter secured to the bottom of the column. The initial solids tested with Leachate A influent were till, tailings and a peat-sand mixture (wet peat:sand mass ratio of 2:1). The till columns were later eliminated (for reasons presented in the results) and the peat-sand beds were replaced by a peat-tailings mixture (wet peat:tailings ratio of 2:1). The Leachate B treatment beds consisted of till, tailings and peat-sand mixture. The bed depths were 25.4 cm for tailings and 38.1 cm for the other solids. Each solid was tested with each leachate in triplicate.

Leachate was delivered to the columns through siphoned flow from four-liter plastic feed bottles, and the effluent was collected at the bottom in two-liter plastic bottles (fig. 5). The beds were initially saturated slowly from below, and subsequent feed was from above at a rate of five bed volumes per day (5 bv/d, one bed volume being the space occupied by the treatment bed). Flow rate was adjusted by a regulator on the effluent discharge tubing. The columns and collection bottles were housed in a plywood cabinet and the feed bottles covered with black plastic so as to minimize light input, and thus biological growth. The Leachate A columns were run until breakthrough was reached. Breakthrough is the point at which the effluent composition is the same as the effluent composition, that is, no additional treatment is occurring. The Leachate B columns were run for six months, and did not reach breakthrough.

Three tailings columns were operated with Leachate B under unsaturated conditions, in addition to the three saturated flow columns, to examine the influences of unsaturated flow. To investigate the effect of flow rate, two additional Leachate A columns, one each with peat-sand and peat-tailings, were run at discharges of 8 to 8.5 bv/d. The impact of slow flow on metal removal from Leachate B was examined by adjusting column flows to a range of 0.5 to 1.5 bv/d near the end of the removal phase.

Following the removal phase, the columns were fed 30 to 230 bv of distilled water to study the release of trace metals. After the completion of the column rinse, two to five bv of 10 pct H_2SO_4 were passed through the columns as a means of examining the economic recovery of the metals.

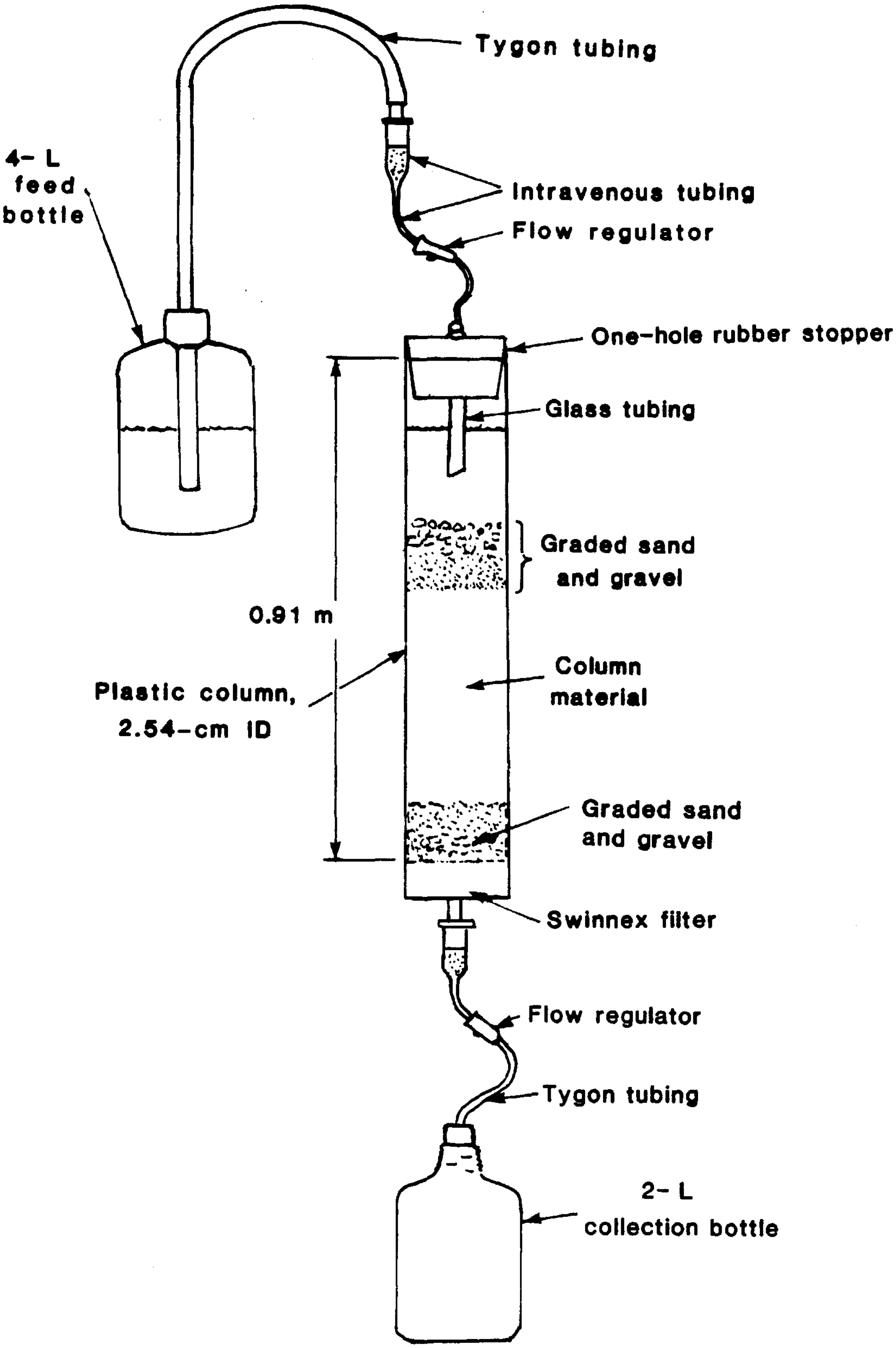


FIGURE 5.- Column experimental design.

Results

The results from each triplicate set of columns were highly reproducible. Of the solids used in the initial tests with Leachate A, the till and peat-sand mixture tended to lower the leachate pH, producing values in the range of 3.9 to 4.1 and 4.9 to 5.3, respectively. Consequently the till columns were eliminated, and the peat-sand mixture was replaced by a peat-tailings mixture which produced both higher effluent pH and lower trace metal concentrations.

The total CEU removal capacity of the Leachate A peat-tailings columns at a flow rate of five bv/d was higher than that for the tailings alone (table 10). Both the peat-tailings and the tailings alone reached breakthrough for Cu, Ni and Co by 230 bv of flow (fig. 6). The peat-tailings achieved maximum CEU reductions of 50 pct, as compared to 82 pct for the tailings alone. The removal of individual metals from Leachate A tended to increase with higher influent levels of that metal. Removal was least for copper and cobalt, which had aqueous concentrations below those of nickel and zinc.

The Leachate B columns did not reach total breakthrough, but the trends observed were similar to those observed for the Leachate A columns. Trace metal removal from Leachate B was greater than that from Leachate A (table 10). Nickel removal constituted 65 to 79 pct of the CEU capacity, and cobalt removal contributed 21 to 36 pct. Copper and zinc removal as a percentage of CEU was negligible.

The initial effluent from the Leachate B peat and till columns had elevated CEU levels and depressed pH. The effluent CEU levels decreased fairly rapidly, reaching a minimum after about 25 to 35 bv of flow. After this point effluent CEU levels varied between about 0.6 and 0.7 mg/L in the peat columns, and from 0.25 to 0.5 mg/L in the till columns (fig. 7). Concurrent with the initial decrease in effluent CEU levels was an increase in pH. Effluent pH from the peat and till columns eventually stabilized at about 7.2 and 6.9, respectively.

The pH of effluent from the tailings columns was fairly stable, typically in the range of 7.0 to 7.4. Trace metal concentrations gradually increased over the first 230 bv of flow. At this point the flow rate decreased from 5 bv/d to 1 bv/d, and trace metal concentrations dropped by about 75 pct. Although trace metal concentrations in effluent from peat and till columns also decreased at this time, the decreases were less dramatic than that observed for the tailings columns.

The unsaturated flow tailings columns had both lower flow rates and effluent metal concentrations than the saturated flow tailings columns. Effluent CEU levels for both types of columns

TABLE 10. - Metal removal capacity of solids as determined at end of column removal phase

Solid	Column	Mass removal capacity, mg/kg dry solid					Total flow volume, bv
		Cu	Ni	Co	Zn	CEU	
				LEACHATE A			
Tailings...	J....	3.3	45.4	1.3	7.3	9.9	252
	K....	2.9	49.2	1.9	7.9	10.5	271
	L....	3.2	48.8	1.4	8.3	10.3	262
	AA[2]..	2.6	50.0	1.8	8.3	10.2	285
Peat-tailings[1].	G....	6.3	78.6	-.3	8.5	14.7	286
	H....	6.2	90.2	-.3	11.3	16.0	267
	I....	6.3	85.0	.1	10.6	16.0	272
	BB[2]..	4.7	71.3	2.1	8.3	14.8	268
				LEACHATE B[3]			
Tailings[4]..	M....	-1.2	451	19.4	15.8	64.9	240
	N....	-.7	490	20.2	13.2	69.8	265
	O....	2.5	620	22.0	9.3	82.4	294
Tailings...	V....	-.9	574	24.0	9.9	81.5	350
	W....	-3.7	533	22.2	14.9	86.7	329
	X....	1.5	721	37.7	28.9	114	938
Peat[5]......	S....	77.7	20,300	699	979	2,900	840
	T....	10.5	16,800	481	962	2,270	539
	U....	0	17,800	546	724	2,400	418
Till.......	P....	1.4	712	21.5	22.7	96.4	389
	Q....	.7	1,020	36.2	34.9	142	718
	R....	.9	829	24.6	20.7	110	394

[1] To obtain removal capacity for wet peat-tailings, multiply by a factor of 0.70.

[2] Average column flow rate was 8.3 bv/d.

[3] Leachate B columns did not achieve total breakthrough.

[4] Unsaturated flow.

[5] Columns contained 90 g wet peat mixed with 180 g sand. It was assumed that all metal removal was accomplished by the peat. To obtain removal capacity for wet peat-sand, multiply by a factor of 0.033.

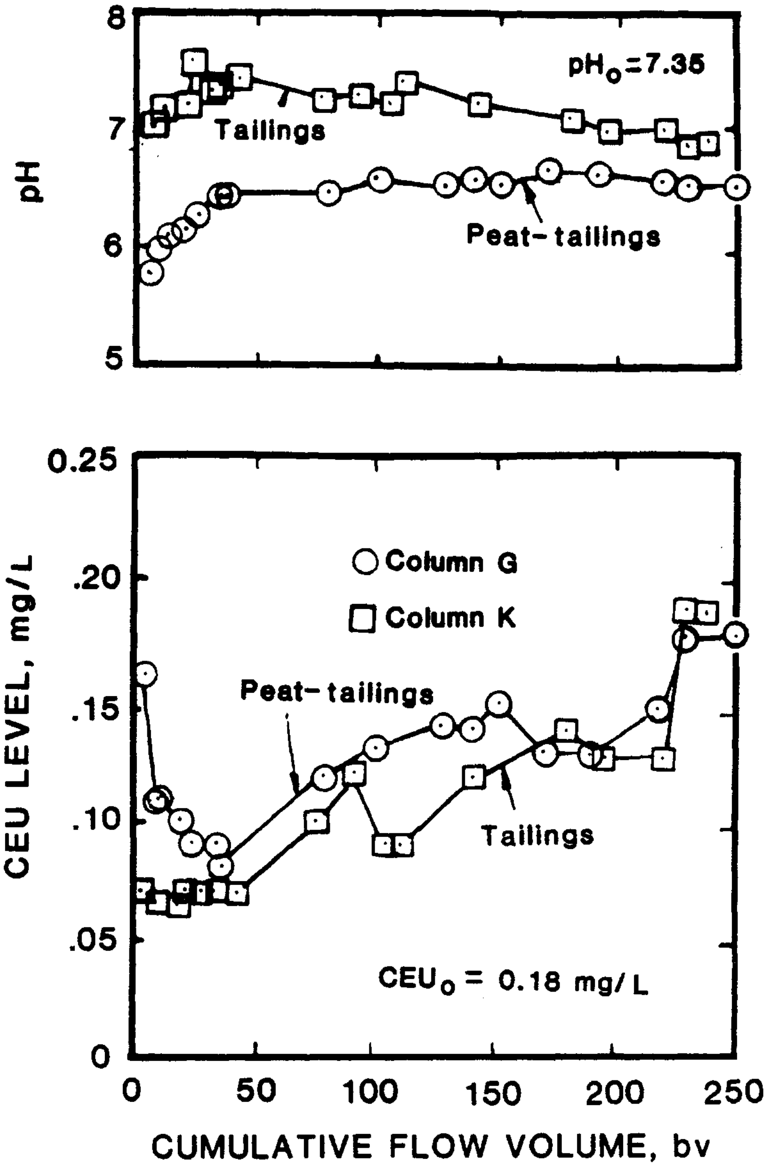


FIGURE 6.- Leachate A peat-sand and tailings columns: pH and CEU level versus cumulative flow volume.

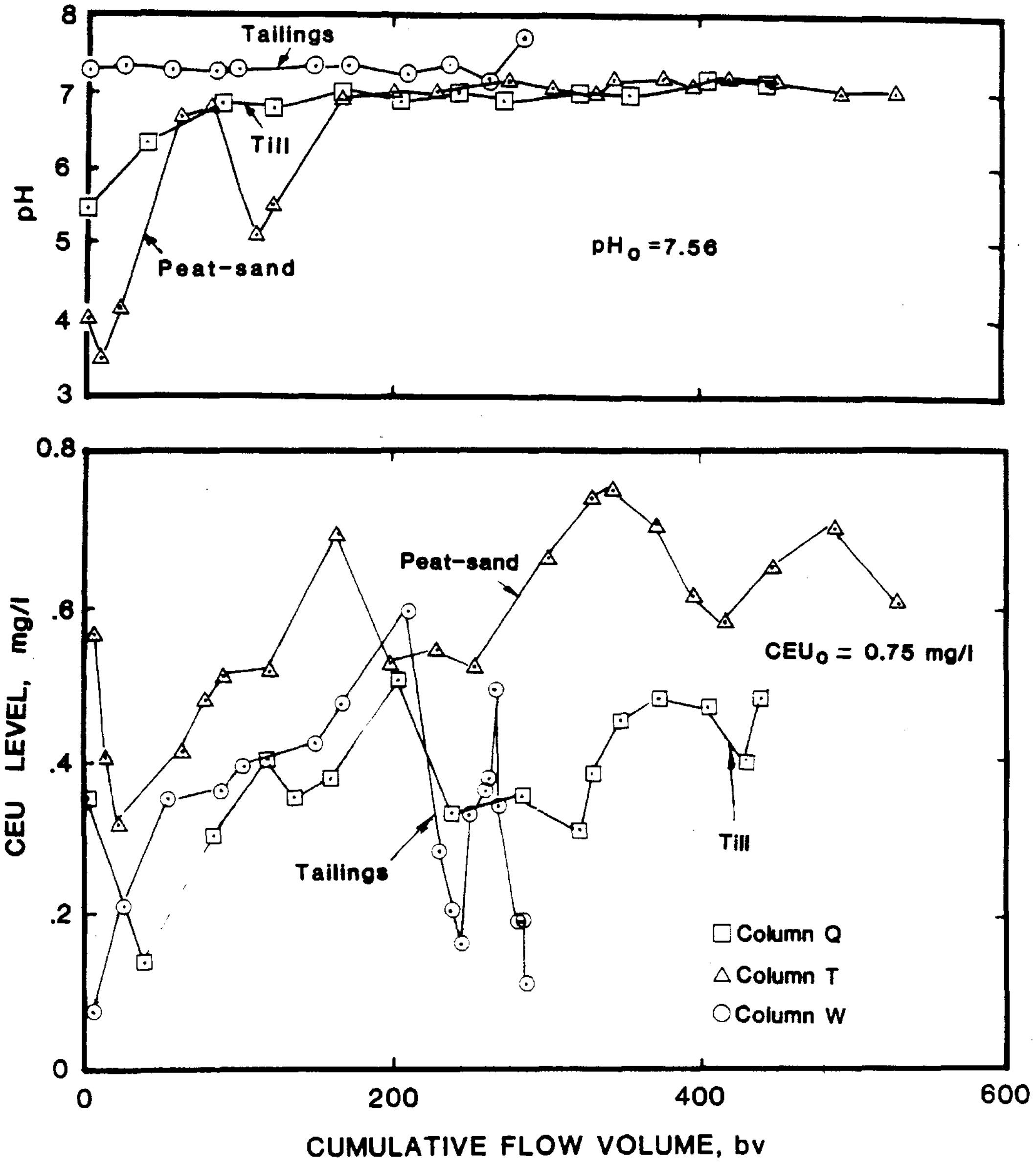


FIGURE 7.- Leachate B saturated flow columns: pH and CEU level versus cumulative flow volume.

decreased as flow rates decreased below 5 bv/d. The effluent CEU decreases also occurred with till and peat-sand, both in experiments designed to examine flow rates and when flow rates decreased unexpectedly. Controlled variation of Leachate A flow rates from 4.7 to 8.3 bv/d, however, did not greatly affect the effluent CEU level from tailings and peat-tailings columns.

The rinse phase results from each set of columns were reproducible, with effluent CEU levels much lower than in the removal phase. Effluent CEU levels were highest initially and decreased rapidly within the first 10 bv of rinse flow. After about 20 bv of flow effluent CEU levels stabilized at 0.01 to 0.02 mg/L for the Leachate A columns and 0.02 to 0.05 mg/L for the Leachate B columns.

Net trace metal removal was calculated by subtracting the mass of metal released in the rinse phase from the mass of metal removed from solution in the removal phase. For all columns metal release was less than 14 pct of the metal removal. Since release was small compared to removal, the trends observed for net removal were similar to those observed for the removal phase. Net removal from Leachate B was about an order of magnitude higher than that from Leachate A, even though Leachate B columns did not reach breakthrough. Net removal from Leachate B decreased in the order till, peat-sand, tailings, and from Leachate A in the order peat-tailings, tailings.

In the recovery phase with 10 pct H_2SO_4, more metals were recovered than were removed in the removal phase. The pH of the recovery solution effluent was typically less than 2, and effluent trace metal concentrations decreased in the order Ni, Cu, Zn, and Co.

Discussion

Column experiments required more time and reaction conditions were less easily controlled than in the batch experiments. However, this type of experiment more closely approximated the leachate-solid contact expected in the field. Column tests allowed determination of metal removal capacities, flow properties of the various solids, and the influence of flow rate on metal removal. The release of attenuated metals to distilled deionized water and to a 10 pct H_2SO_4 solution was also examined.

The breakthrough curves generated by column data were not the classical S-shaped curves commonly reported in this type of experiment. Effluent concentrations tended to rise gradually and plateau for extended period, perhaps due to the generation of fine particles within the bed.

One clear pattern in effluent metal levels was an abrupt decrease in concentrations from Leachate B till and tailings columns after 38 to 57 days of flow. This decrease seemed to result from a relatively sudden and uncontrolled decrease in flow rates, from an average of 4.3 bv/d to 0.97 bv/d. The decrease in flow rates, in turn, was due to dissolution of the bed solids and subsequent precipitation of fine particles. After seven of the till and tailing columns were dismantled, resieved to remove the less than 75 um size fraction, and reassembled, column flow rates increased from an average of 0.81 bv/d to over 5 bv/d. The fine tailings fraction removed in the resieving averaged 34 pct of the bed mass. Sieve tests demonstrated that up to half of these fines may have resulted from insufficient sieving time at the beginning of the experiment. Scanning electron microscope (SEM) analyses indicated a change in the plagioclase line profile between the leached and unleached tailings samples. The leached tailings fraction contained halloysite, which was absent in an unleached sample of the same size fraction. Halloysite has been reported as a early stage dissolution product of plagioclase (13) and other feldspars (37, 134). Other layered silicate clay minerals, as well as iron oxides, hydroxides, and oxyhydroxides can be products of silicate mineral dissolution (37, 92, 134). Aluminum hydroxide reaction products have been reported, but are common only in highly weathered regions such as those of the tropics.

Precipitation of fine reaction products most likely affected the observed decrease in flow rate and the reduction in effluent trace metal levels. After the fine fractions were removed from the seven previously mentioned columns, effluent trace metal levels as well as flow rate increased. Many layered silicates, as well as most oxides and hydroxides of iron, can adsorb significant amounts of trace metals from solution (20, 53, 65, 119, 122, 131). Dissolution of the original tailings material would have produced these solids capable of metal adsorption. Thus, the generation of fine reaction products within the column beds would tend to have reduced both flow and effluent metal concentrations.

The precipitation of fines may explain the failure of the Leachate B columns to achieve total breakthrough. The elevated organic content of Leachate B relative to Leachate A may have accelerated silicate mineral dissolution in the Leachate B columns (58, 59, 108); other differences in solution composition may also have affected the silicate dissolution rate (1, 68). This dissolution would have generated reaction products capable of additional adsorption, thereby continually increasing the trace metal removal capacity in the Leachate B columns.

In the Leachate B flow rate experiment, the flow rate was reduced by manual adjustment rather than by precipitation of fines, and a reduction in effluent metal levels was again observed. The lower effluent concentrations may have been due to increased contact time or more uniform flow through the bed. At a flow rate of 1 bv/d, the contact time between the solution and solids would have been five times that at a flow rate of 5 bv/d.

In the kinetics batch tests, trace metal concentrations of Leachate B had continued to decrease after 24 h of reaction with tailings. Similarly, metal removal may have increased due to the increased reaction time available at slower flow rates in the columns.

Increased contact time would also have enhanced metal removal if flow occurred along preferential paths rather than uniformly throughout the bed. If such flow occurred, adsorption sites along preferential paths would have been occupied by metals while sites remote from the flow would have been relatively free. At slower flow rates the influence of diffusion away from the preferential paths would have increased (76, 127). Thus, the slower rates would have allowed a greater fraction of the available adsorption sites to participate in metal removal. Slower flow rates would also have tended to cause more uniform flow throughout the bed. Thus the generation of fine particles may have further reduced effluent trace metal levels by: 1) increasing the number of adsorption sites; 2) allowing additional time for removal reactions and diffusion; and 3) bringing about more uniform flow through the bed.

The difference in effluent trace metal concentrations between the Leachate B saturated and unsaturated tailings columns can be explained solely on the basis of flow rate differences. The unsaturated columns had lower average flow rates in part due to the difficulties in maintaining a constant flow rate.

Factors in addition to silicate precipitation, such as sulfide precipitation, biological growth, temperature change and/or bed compaction, may have been responsible for lowering effluent metal levels and/or slowing column flow rate. Development of anaerobic conditions within the columns, with subsequent metal sulfide precipitation, would have reduced effluent concentrations; this process would seem to have been unlikely, however, in columns of 25 to 38 cm length. The only significant biological growth detected in the columns was small amounts of fungi in the gravel at the ends of the beds, although the fungi were not widespread enough to impede flow. Significant increases in lab temperature were associated with the previously mentioned uncontrolled slowdown in Leachate B columns; such temperature variation did not occur, however, in a similar slowdown during the rinse phase. Bed compaction was evident in all columns, although compaction was greater than 2.5 pct only in the peat-tailings, peat-sand and one of the till columns. Compaction could have both slowed the flow rate and decreased pore volume.

As was the case in batch experiments, till and peat tended to depress solution pH; and metal removal was a function of solution pH and trace metal concentration. With Leachate A, the till and peat-sand mixture produced low effluent pH and were rejected for use. The buffering capacity of the tailings was adequate to neutralize the acidity of the peat when these solids were mixed. The peat-tailing mixture produced an effluent of higher pH and lower trace metal concentrations than the peat-sand effluent. With Leachate B, the peat and till columns produced an effluent which initially had low pH and elevated trace metal concentrations. However, the alkalinity of this leachate was about three times that of Leachate A, and effectively neutralized the acidity of these solids after 20 to 40 bv of flow.

Metal removal from both leachates tended to increase with increasing aqueous metal concentrations. With both leachates, nickel was the dominant trace metal in solution and exhibited the greatest mass removal. Metal removal from Leachate A was lowest for copper and cobalt, and aqueous concentrations of these metals were lower than those of cobalt and zinc. The removal of metals from Leachate B followed the same order as the aqueous metal concentrations, decreasing in the order Ni, Co, Zn, and Cu.

The mass of materials required for treatment was calculated as follows. A maximum acceptable effluent CEU level was established based on bioassay tests of column effluent (79). The volume of effluent (in bv) with CEU levels below this limit was then determined for each solid. The projected annual runoff was then divided by the number of bed volumes to obtain the mass required for field treatment. This calculation assumed that the bulk density of the materials in the field would be the same as in the columns. Waste rock stockpiles (325 x 10^6 mt) covering an area of four square kilometers would generate about 1.5 x 10^9 L of drainage in a year of average precipitation (56, 130). For 1.5 x 10^9 L of Leachate B-type runoff and a maximum allowable effluent CEU level of 0.28 mg/L (close to 0.29 mg/L, the concentration in Leachate B tailing column effluent that corresponded to a 48-h LC50 in the bioassay test), 32,000 mt of till or 84,000 mt of tailings would be required. One of the three peat-sand columns did not produce effluent below 0.28 mg/L CEU; data from the other two columns yielded a value of 6,400 mt of dry peat required to produce effluent at or below 0.28 mg/L CEU. Although the mass of dry peat required was less than that of tailings, on a wet basis the amount of peat needed would increase by about a factor of ten.

The mass of tailings of diameter greater than 75 um generated in a model operation would be 6.5 x 10^7 mt, assuming a 2:1 mass ratio of waste rock to tailings and that 40 pct of the tailings are larger than 75 um. Thus, despite the comparatively low metal removal capacity of the tailings, the mass available represents the potential for removing large quantities of trace metals from waste rock stockpile drainage. Tailings are also attractive since their disposal is part of the mine plan.The use of other solids would create an additional waste disposal problem. Tailings were thus selected over peat and till as the principal solids to be investigated in subsequent field tests.

The column rinse phase results indicated that the materials can retain metals in a dilute solution. The influent tested in the lab was distilled deionized water, which in a field setting would correspond to non-acidic rainfall and/or snowmelt. The low effluent concentrations encountered in the rinse phase suggested that there would be relatively low release levels in a field situation. However, the batch rinse experiment showed that a solution of lower pH, such as acid rain, would result in higher levels of metal release.

The column recovery test with 10 pct H_2SO_4 did not appear to yield enough metals to make such a process economically worthwhile. Based on the market f.o.b. values of the four metals in 1983 (33), \$2 to \$30 worth of metals were recovered per ton of bed material. In general, the metal mass recovered from the column beds exceeded the mass removed from the leachates in the removal phase. This indicated that some of the metals originally present in the solid were leached by the acid.

FIELD EXPERIMENTS

Unsaturated Bed

Methods

Inflow to the bed was supplied by drainage from a copper-nickel rock stockpile denoted FL1 (29). The drainage was pumped through a flow splitter to two polyethylene barrels designed to moderate pump surges (fig. 8). One of the barrels drained to a saw-tooth weir at the end of the unsaturated bed housing, which was 4.9 m long, 0.30 m wide and 1.22 m deep. It was separated into seven compartments by dividers, which were 7.6 cm high, placed across the bottom of the bed. Lengths of perforated PVC pipe were placed across the center of each compartment for collection and discharge of effluent. Approximately 2,000 kg of tailings were added, giving an initial bulk density of 1.5 to 1.6 g/cm^3 and porosity of 45 to 47 pct. Some bed compaction occurred during 1982, but the bulk density did not exceed 1.7 g/cm^3. To dissipate energy from the input, a 5-cm length of Mirafi mesh was placed directly below the weir, a stiff plastic screen was placed over the first 0.91 m of the bed (below the weir), and a single particle depth of pea rock was placed over the first 0.3 m. Below the weir, 10 ceramic sampling cups were installed to sample water quality at four different depths. These samples were collected on eight occasions in 1982. In June 1983 manometers were installed in each segment to measure water levels within the bed.

The cumulative flow volume from the FL-1 stockpile and the unsaturated bed ports was determined from the Badger Recordall meters; more precise timing of flows was obtained from Rustrak event recorders (model 292-4, 29). The FL-1 flow-weighted composite water quality samples were typically collected weekly. In 1982 composites were collected from the unsaturated bed at approximately 2, 5, 10, 15, 20, 25, and 30 bv of cumulative flow, and at approximately 10-bv intervals subsequently. In 1983 water quality samples from all segments were composited over the same time intervals, and corresponded more closely to the FL-1 input samples.

Results

The unsaturated bed received stockpile flow for 63 days in 1982 and for 100 days in 1983, when flow was split with the saturated bed. Segment seven was not equipped with a flow meter during the first season but rather with a sump which was measured by field inspection. Although this segment did not receive much flow, problems were encountered when input exceeded about 1,500 L/d and the sump would overflow. When the drain pipe was removed from the sump, discharge increased, suggesting that the filled sump caused an additional resistance to draining the seventh

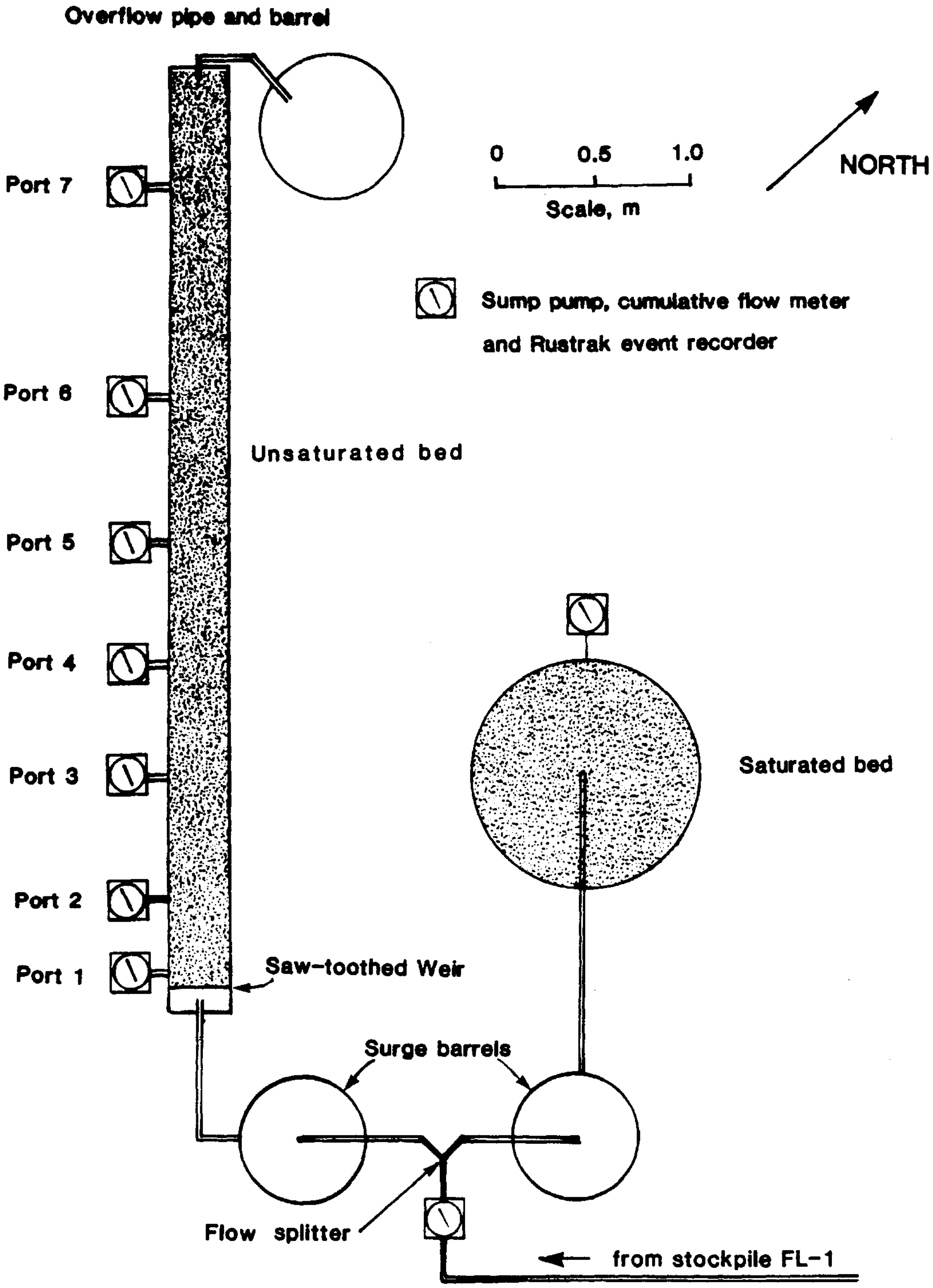


FIGURE 8.- Tailings treatment beds, top view.

segment. This may also have affected flows from the fifth and sixth segments when input exceeded 1,500 L/d. A flow meter was installed on the seventh segment before the 1983 season to rectify this problem.

The input flow rates ranged from 17 to 3,900 L/d, providing a total input of 49,000 L. Over half the time flows were less than 100 L/d, but these flows accounted for only 20 pct of the input volume. In contrast, flows exceeding 1,000 L/d contributed 37 pct of the input volume but occurred only 6 pct of the time. The seasonal average flow rate in 1983 was less than half that in 1982, but the maximum flows in both years occurred during October.

The amount of flow passing through the bed decreased as distance from the input weir increased. For input flows of 50 to 140 L/d, 80 to 90 pct of the output occurred within the first 0.76 m of the bed. As the input flow increased, output was observed at more distant segments. To normalize for the variation in segment lengths, the vertical hydraulic loading (specific discharge) for the segments was calculated; the observed discharge from each port was divided by the horizontal cross-sectional area of the segment draining to the port. The hydraulic loadings increased as input flow increased and were typically highest near the input weir (table 11). One exception to this observation was the behavior of the first two segments at low flows, particularly when input was less than 100 L/d in 1983. At these times the hydraulic loading of the second segment often equalled or exceeded that of the first segment.

In both years the capacity of the bed was exceeded in October, and flow passed through the overflow outlet. During these periods a maximum capacity of about 4,200 L/d was determined for the bed. This implies a maximum hydraulic loading of 3.3 x 10^{-3} cm/s, when the water was ponded to a depth of 28.6 cm. Using these values in conjunction with bed depth, the saturated hydraulic conductivity of the bed was calculated as 2.5 x 10^{-3} cm/s. It is unlikely that the bed was actually saturated since water levels never rose in the manometers during the 1983 season.

Discussion

Over the two seasons the metal input to the bed was 70 g CEU. Nickel contributed about half the input CEU, while copper and cobalt contributed 26 and 22 pct, respectively. The influent CEU levels ranged from 0.4 to 2.5 mg/L, and pH from 6.3 to 7.15. In both years the maximum metal concentrations occurred in September, and the majority of metal input occurred during periods of high flow.

The trace metal mass input in 1983 was higher than that in 1982, despite the observed decrease in input flow volume. This increase was due to an increase in metal concentrations. Copper

TABLE 11. - Hydraulic Loading in Unsaturated Bed, Selected Flow Periods

Flow period	Inflow, L/d	Hydraulic loading, 10^{-6} cm/s						
		Segment 1	Segment 2	Segment 3	Segment 4	Segment 5	Segment 6	Segment 7
1982								
9/14,10:30- 9/16,24:00..	496	2,080	1,310	902	306	18.8	54.6	NA
9/16,24:00- 9/18,14:00..	783	2,570	1,920	1,420	846	304	129	NA
9/18,14:00- 9/20,20:00..	438	1,870	1,560	764	226	0	38.8	NA
9/20,20:00- 9/23,05:00..	247	1,300	970	362	97.3	0	0	NA
10/ 8,06:00-10/ 9,17:00..	1,060	2,600	1,910	1,720	1,170	725	259	NA
10/ 9,17:00-10/10,23:00..	3,260	3,490	2,470	2,140	2,330	1,960	4,050	NA
10/10,23:00-10/11,24:00..	1,280	2,680	2,020	2,090	1,510	1,200	837	NA
10/11,24:00-10/13,05:00..	927	2,210	2,000	1,800	995	399	193	NA
10/13,05:00-10/14,16:00..	612	2,200	1,580	1,180	413	99.2	0	NA
10/14,16:00-10/20,16:00..	287	1,190	927	473	131	8.0	4.8	NA
1983								
5/27,08:00- 6/ 2,08:00..	134	683	553	58	20	4	17	0
6/ 2,08:00- 6/ 9,10:00..	39	100	190	6.9	5	3	10	0
6/ 9,10:00- 6/13,07:50..	17	100	62	0	3	6	7	0
8/18,08:40- 8/22,08:05..	67	270	306	13	9	5	0	8.7
9/ 7,08:25- 9/ 8,08:30..	41	150	220	0	0	0	0	0
9/23,08:10- 9/28,08:40..	42	180	190	0	8	17	0	0
10/ 4,09:05-10/11,08:20..	389	1,530	1,480	395	180	82	3.8	21
10/12,08:35-10/14,10:30..	234	1,100	947	130	50	36	0	0
10/17,08:40-10/18,09:40..	306	1,500	1,210	210	40	74	0	0
10/18,09:40-10/21,08:10..	192	1,000	804	93	0	0	2	0
10/24,08:35-10/27,08:30..	56	250	230	22	0	0	0	2

NA Not available.

NOTES. - 1983 inflow data are estimated based on sum of output from all seven segments. Hydraulic loading data for segment four from 5/27 to 10/14 are estimated based on values from other six segments.

concentrations increased by a factor of 3.5, while nickel and cobalt concentrations increased by a factor of 1.5. Thus, the fraction of CEU contributed by copper increased, while the relative contributions of the remaining metals decreased. In addition, the pH in 1983 was slightly lower than that observed in 1982.

The total output from the unsaturated bed was 40 g CEU, indicating a 42 pct removal. Effluent CEU levels, although lower than influent levels, tended to follow similar seasonal trends. They were low initially, reached a seasonal maximum in September, and subsequently decreased. The reduction of influent levels decreased over time, as indicated by data from segment 1 (table 12). Effluent CEU levels tended to decrease (fig. 9), and pH increased with increasing distance from the input.

Nickel contributed about 70 pct of the output CEU, while cobalt and copper contributed 25 and 5 pct, respectively. The metal removals per unit mass tailings for copper, nickel, cobalt, zinc, and CEU were 9, 56, 4 2, and 18 mg/kg. Although the mass of nickel removed was over three times that of the other metals combined, the fraction of nickel removed was lowest at 41 pct. The behavior of Ni, Co and Zn was similar to that observed for CEU. Effluent concentrations tended to parallel influent concentrations, and removal of these metals decreased over time (tables 12, 13). Their removal in 1983, in terms of mass and percentage, was considerably lower than that observed in 1982. Effluent concentrations typically decreased with increasing distance from the weir. One exception occurred in 1983, when output concentrations of these metals from segment 2 were regularly higher than those from segment 1. As time passed there was less variation in effluent Ni, Co and Zn concentrations from the various segments. Near the end of the study, concentrations from the first four segments approached influent levels.

The overall copper removal of 89 pct was the highest of the four metals examined, although its mass removal was second to that of nickel (table 13). The removal was fairly constant over time, with effluent copper concentrations ranging from 80 to 93 pct of influent concentrations (table 12). Effluent concentrations were higher in 1983, but were fairly constant within each season. They were also fairly constant with respect to distance from the weir, decreasing only slightly as distance increased.

Aqueous trace metal concentrations tended to decrease with depth in the bed, the largest decrease occurring within the top 20 cm of the bed. Subsequently, copper and nickel concentrations were relatively constant, while cobalt and zinc concentrations tended to decrease further. The cobalt decrease was most noticeable during the first two sampling periods, while zinc concentrations decreased with depth up to the final sampling. Solution pH typically increased with depth throughout the study.

TABLE 12. - Reduction in Metal Concentrations at Port One, Unsaturated Bed

Input period	Output period	Cumulative flow volume, bv	pH		Concentrations in mg/L														
					Cu			Ni			Co			Zn			CEU		
			In	Out	In	Out	Pct reduction	In	Out	Pct reduction	In	Out	Pct reduction	In	Out	Pct reduction	In	Out	Pct reduction
								1982											
7/26- 8/ 2	7/18- 7/30	5	7.1	7.4	0.08	0.02	75	2.52	1.05	58	0.11	0.02	82	0.07	0.02	71	0.45	0.15	67
8/ 2- 8/ 9	7/30- 8/ 9	10	7.0	6.5	.09	.02	78	3.40	2.03	40	.15	.04	73	.07	.02	71	.59	.26	55
8/ 9- 8/16	8/ 9- 8/30	16	7.0	7.2	.10	.02	80	5.17	3.48	33	.22	.12	45	.09	.03	67	.85	.49	42
8/30- 9/ 8	8/30- 9/ 8	20	6.9	7.1	.12	.02	83	5.94	3.87	35	.27	.13	52	.12	.03	75	1.00	.54	46
9/ 8- 9/13	9/ 8- 9/13	25	6.5	7.8	.28	.02	93	7.89	2.90	63	.37	.12	68	.15	.03	80	1.45	.43	70
9/13- 9/20	9/15- 9/20	41	6.5	6.8	.19	.03	84	7.35	5.05	31	.28	.17	39	.14	.08	43	1.22	.71	42
9/20- 9/23	9/20- 9/23	41	6.9	6.9	.19	.02	89	7.30	5.63	23	.29	.19	34	.14	.12	14	1.22	.78	36
10/ 4-10/11	10/ 4-10/11	61	7.0	7.3	.18	.03	83	6.17	4.40	29	.30	.17	43	.11	.08	27	1.11	.65	42
10/11-10/18	10/11-10/18	73	6.8	6.7	.11	.02	82	4.57	3.41	25	.15	.14	7	.08	.07	12	.72	.51	29
10/18-10/25	10/18-10/27	78	NA	7.1	.11	.02	82	4.39	3.11	29	.17	.11	35	.08	.08	0	.73	.45	38
								1983											
5/24- 6/10[1]	5/24- 6/10	86	7.0	7.2	.07	.01	86	3.7	1.1	70	.15	.05	67	.11	.02	82	.61	.17	72
8/16- 8/26[1]	8/16- 8/26	92	6.6	6.75	.82	.04	95	11	12	- 9.1	.47	.47	0	.38	.29	29	2.4	1.7	29
8/26- 9/ 8[1]	8/26- 9/ 8	100	6.7	7.0	.59	.04	93	8.7	6.5	25	.38	.27	29	.32	.25	22	1.9	.98	48
9/ 8- 9/22	9/ 8- 9/22	109	6.7	6.75	.83	.06	93	12	8.4	30	.50	.34	32	.39	.27	31	2.5	1.3	48
9/22-10/ 5[1]	9/22-10/ 5	121	6.8	6.7	.56	.08	86	8.6	10.3	-20	.38	.42	-11	.26	.36	-38	1.8	1.6	11
10/ 5-10/12	10/ 5-10/12	132	6.9	6.8	.52	.07	86	8.1	8.5	- 4.9	.34	.34	0	.26	.26	0	1.7	1.3	24
10/12-10/20	10/12-10/20	142	6.9	6.8	.45	.05	89	7.8	7.7	1.3	.31	.30	3.2	.24	.22	8.3	1.6	1.1	31
10/20-10/27	10/20-10/27	145	6.9	6.75	.39	.07	82	7.2	8.1	-12	.28	.32	-14	.24	.24	0	1.4	1.2	14

NA Not available.

[1] Flow weighted mean of two composite samples.

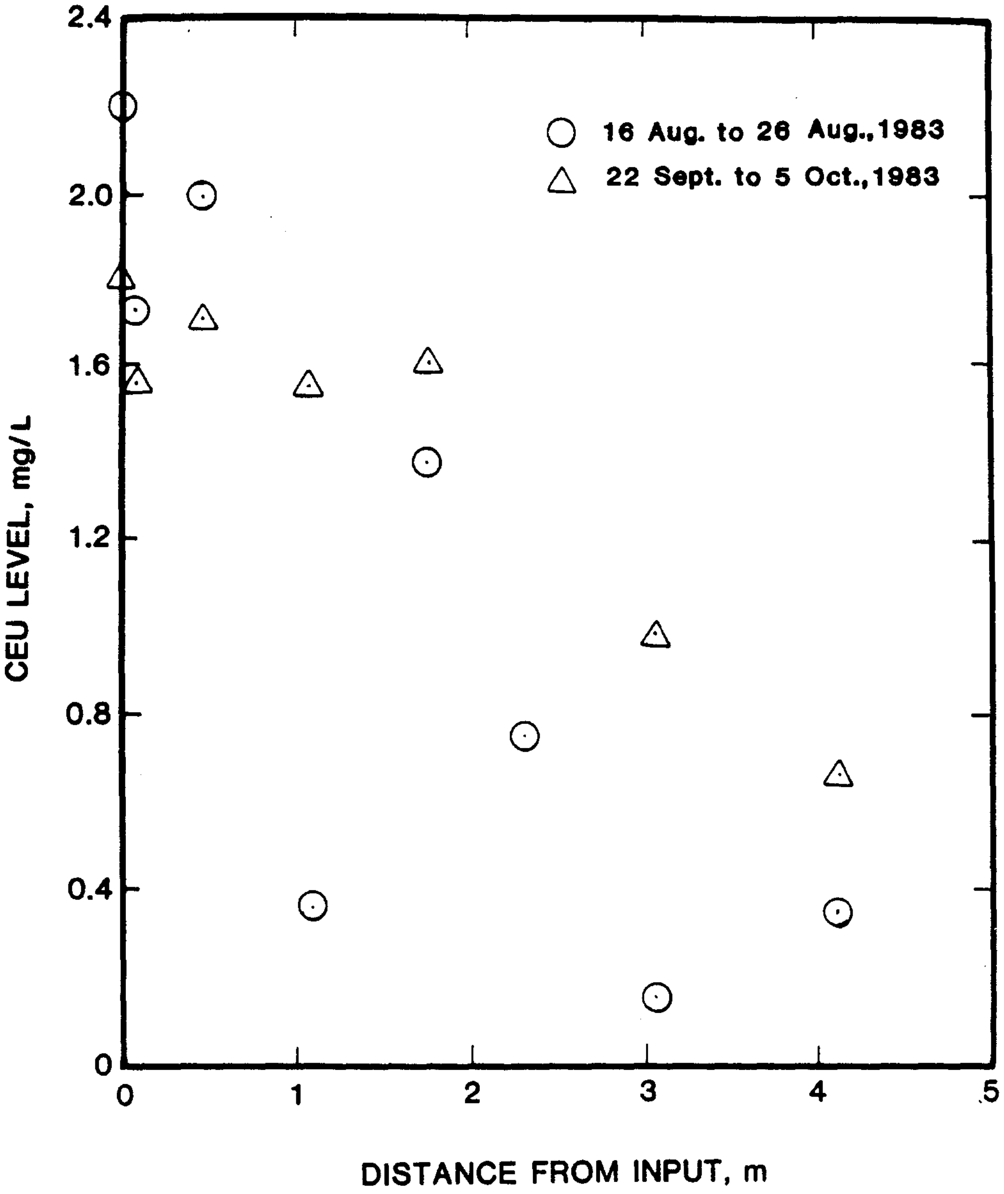


FIGURE 9.- Variation in CEU level of unsaturated bed effluent with distance from input.

TABLE 13.- Metal Removal by Unsaturated Bed

Metal	Mass, g			Pct removal	Removal per mass of tailings, mg/kg
	Input	Output	Removal		
			1982		
Cu.....	4.7	0.65	4.05	86	2.8
Ni.....	169	100	69	41	48
Co.....	7.3	3.0	4.3	59	3.0
Zn.....	3.1	1.4	1.7	55	1.2
CEU....	29	14	15	52	10
			1983		
Cu.....	13	1.3	11.7	90	5.8
Ni.....	190	173	17	9	8
Co.....	8.0	6.5	1.5	19	0.8
Zn.....	6.3	4.9	1.4	22	.7
CEU....	41	26	15	37	7
			TOTAL		
Cu.....	18	1.95	16	89	8.6
Ni.....	359	273	86	24	56
Co.....	15.3	9.5	5.8	38	3.8
Zn.....	9.4	6.3	3.1	33	1.9
CEU....	70	40	30	43	18

NOTE. - 1982 output data are for ports one to six, while 1983 output data are for ports one to seven.

In order to relate bed discharge to input flow and the distance of the output from the input, a flow model was constructed. The inputs to given segment of the bed, segment i, include a surface component (R_i), a subsurface component (G_i), and a precipitation component (P_i). In addition to discharge from the bed at the base of the segment (D_i), the outputs from the segment include a surface component (R_{i+1}), a subsurface component (G_{i+1}), an evapo- ration component (E_i). The water balance for a given component can then be expressed as follows:

$$R_i + G_i + P_i = D_i + R_{i+1} + G_{i+1} + E_i + \quad S_i, \tag{5}$$

where S is the change in storage and all quantities are expressed in the same volume per unit time.

The surface and subsurface components are combined into one flow component in the x direction (that is, $R_i + G_i = Q_i$). Furthermore precipitation, evaporation and change in storage are assumed to be negligible with respect to other flows. Thus, equation 5 reduces to:

$$R_{i+1} + G_{i+1} = Q_{i+1} = Q_i - D_i \tag{6}$$

The assumption of negligible storage implies a steady-state condition. It is also assumed that the bed material was homogeneous, and that the walls surrounding the bed do not have a significant effect on flow.

The model was constructed based on data from 10 periods in 1982, ranging from 25 to 144 h in length. The periods selected were those during which inflow and outflow data were complete, and flow approximated steady state. The following equation was selected to express the hydraulic loading of the first segment as a function of input flow:

$$L = L_{max}BQ_o/(1 + BQ_o) \tag{7}$$

where L = hydraulic loading of the first segment in cm/s,
L_{max} = the maximum hydraulic loading in cm/s, and
Q_o = input flow in cm^3/s, and B is a constant in s/cm^3.

This approach is similar to models that relate the unsaturated hydraulic conductivity to the saturated conductivity and moisture content (9, 71).

Ten ordered pairs (L_i, $Q_{o,i}$) were then determined for the first segment during various time periods in 1982. Linear regression analysis was then conducted for a plot of L versus L/Q_o (24), and values of 3.8 x 10^{-3} cm/s and 2.1 x 10^{-3} s/cm^3 were determined for L_{max} and B, respectively (r^2 = 0.79). The L_{max} value implies a maximum hydraulic loading of 3.8 x 10^{-3} cm/s. The maximum hydraulic loadings observed for the entire bed and segment one were 3.3 x 10^{-3} cm/s and 4.0 x 10^{-3} cm/s. Both of these values occurred when the bed was ponded and overflowing. The hydraulic conductivities associated with these values were calculated as 2.5×10^{-3} and 2.9×10^{-3} cm/s, respectively. These values were higher than the 2.2×10^{-4} to 8.8×10^{-4} cm/s range determined at similar bulk densities in the laboratory (table 4).

This information was extended to the remainder of the bed by assuming subsequent segments would respond to input flow similar to the first segment. To determine the input (Q_i) to one of these segments, the output from preceding segments must be determined. The desired input can then be determined by subtracting this output from the initial input.

The mathematics of this concept are cumbersome and it is necessary to first solve for x, the distance from the weir (cm), for given values of Q_o and Q_i:

$$x_i = -[\ln(Q_i/Q_o)/B+Q_i-Q_o]/L_{max}z + C_1 \tag{8}$$

where z is the bed width (cm) and C_1 is a constant determined by boundary conditions. In this case C_1 = 7.6 cm. Using this equation for a given bed input (Q_o) and selecting a smaller value for Q_i, the distance (x_i) at which that input occurs can be determined. Inserting Q_i and the previously determined values of L_{max} and B into equation 7 will yield the hydraulic loading at x_i.

The model closely approximated the values observed in 1982 for inputs as high as 1,000 L/d (fig. 10). The deviation was slightly greater for an input of 1,300 L/d and quite large when input reached 3,300 L/d. The flow impedance at the seventh segment outlet, and the influence of the wall at the end of the bed most likely contributed to the deviation at high input flows.

Comparison of the 1983 results with those of 1982 was difficult because the 1983 inputs were typically much lower. Only 2 of the 11 periods in 1983 had inflows greater than the minimum 1982 value used, and only 5 periods had inputs greater than 100 L/d (table 11). The flow data for these periods generally conformed well to the model developed from the 1982 data. Flow data from periods during which the inflow was less than 100 L/d did not fit the model curves as closely. The discharge from the bed during these periods was fairly evenly distributed between segments one and two, rather than being concentrated in the first segment as the model indicates.

This deviation may have been influenced by the drier bed conditions generally associated with low flow and/or the materials placed beneath the weir to dissipate the energy of the input flow. Under dry conditions the ratio of lateral to vertical water movement tends to be higher than under wetter conditions (57). The enhanced lateral movement would tend to provide a greater fraction of flow to the second segment. The nylon mesh, plastic

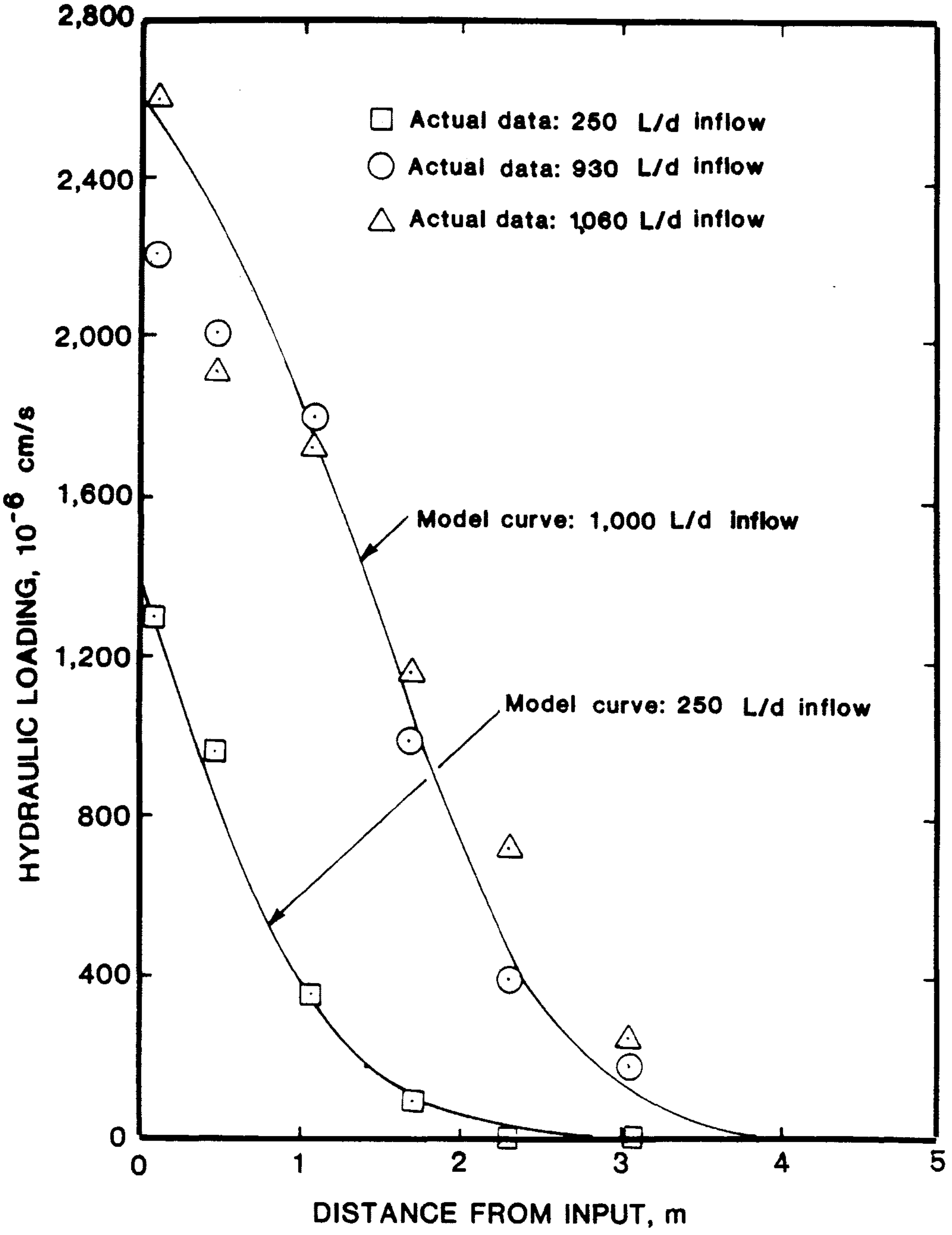


FIGURE 10.- Outflow model curves and 1982 data for unsaturated bed inflows of 250 and 1,000 liters/day.

screen, and pea gravel placed above the tailings surface beneath the weir may have also contributed to the deviation. These materials, particularly the nylon mesh, may have encouraged lateral flow and/or inhibited vertical flow when input was low.

Another possibility, although less likely, is that the hydraulic conductivity of the first segment decreased from 1982 to 1983. Such a decrease was observed with tailings used in laboratory column experiments, and was attributed to the generation of fine particles by tailings dissolution. Compaction of tailings in the first segment would also contribute to such a decrease. These effects would be most probable in the first segment, which received flow continuously over the study. However, a decrease in hydraulic conductivity would also decrease hydraulic loadings at higher input flows, and this was not observed.

Periods of bed overflow occurred in both 1982 and 1983, and the hydraulic loadings for segment one were 4.0×10^{-3} and 4.2×10^{-3} cm/s, respectively. These values were slightly higher than the average hydraulic loading for the entire bed, which during both overflow periods fell in the range of 3.2×10^{-3} to 3.4×10^{-3} cm/s. This further suggests that the hydraulic conductivity of the first segment did not decrease even though it received continuous flow.

Saturated Bed

Methods

The saturated flow tailings bed was assembled in October 1982 and functioned throughout the 1983 flow season. A linear polyethylene tank, 0.95 cm thick, 2.1 m high and 1.2 m in diameter, contained the bed. The drainage was collected through slots on the bottom of 12 radiating PVC pipes (1.9-cm ID) and fed to a 10.2-cm hub (fig. 11). The drainage collection assembly was set in 15 cm of pea gravel, above which a sheet of Mirafi 140S nylon mesh was placed (fig. 11). Approximately 1,300 kg of tailings were placed to a height of 60 cm above the mesh, yielding an initial bulk density of 1.9 g/cm^3 and porosity of 35 pct. The depth of tailings, and thus also the bulk density and porosity, did not change noticeably over the course of the study. A second sheet of Mirafi was placed on the tailings surface to prevent scouring by the inflow.

Inflow to the saturated bed was provided by drainage from copper-nickel test stockpile FL-1, the same source supplying the unsaturated bed (fig. 8). Flow from the surge barrel drained through three outlets into a PVC pipe, which then discharged just above the tailings surface (fig. 11). The discharge from the bed was directed to a sump equipped with a cumulative flow meter and a Rustrak event recorder, as well as an automatic device that took composite samples for water quality analysis.

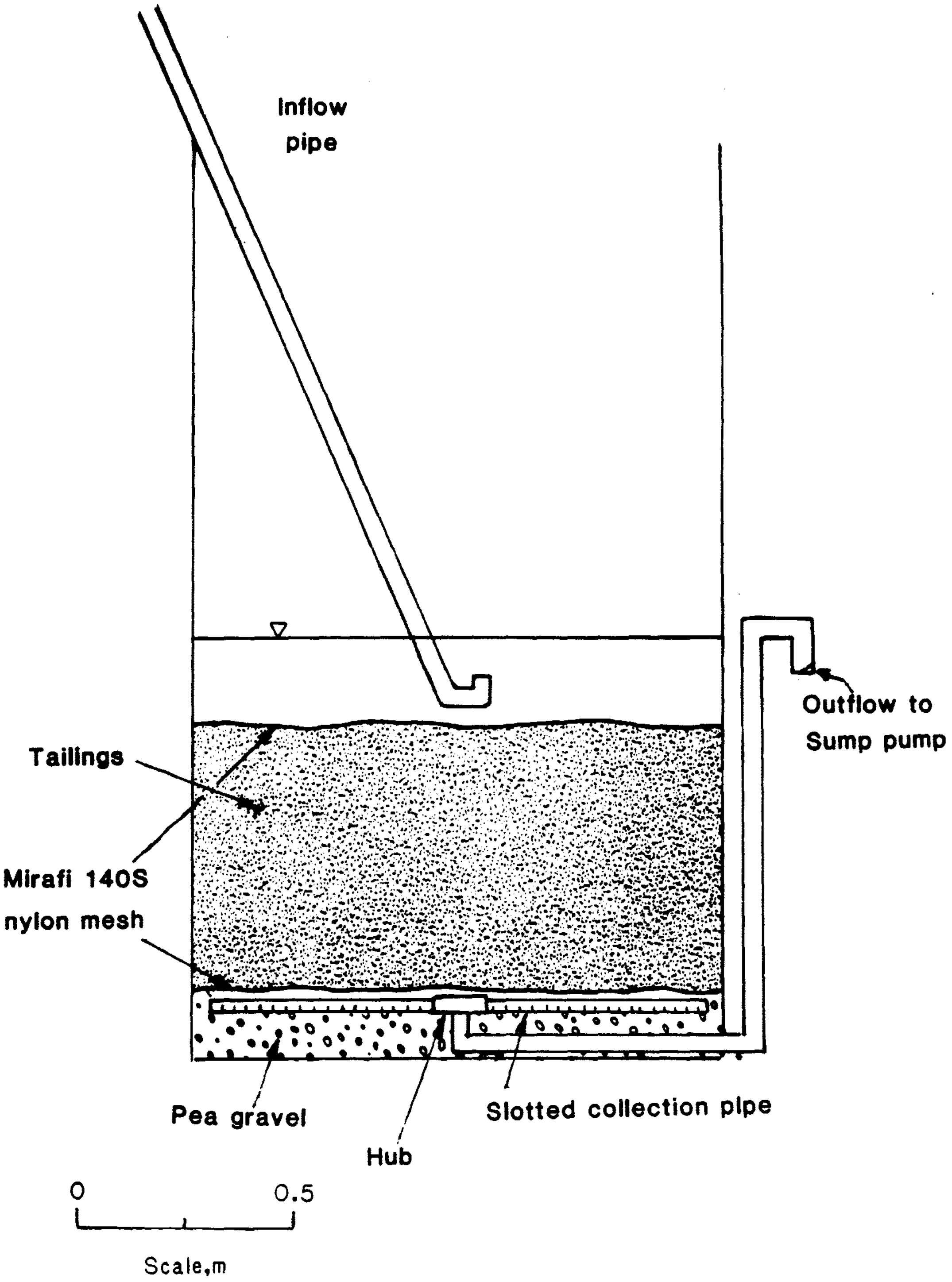


FIGURE 11.- Saturated flow tailings bed, cross-section.

Results

The saturated bed operated from 16 May to 27 October 1983. The inflow from FL-1 drainage was split between the saturated and unsaturated beds (fig. 8) during most of this period. The saturated bed received all FL-1 inflow, however, between 17 June and 16 August. A total of 44,000 L of stockpile leachate passed through the saturated bed at flow rates from near zero to over 2,600 L/d. A lag time of less than one day separated peak inflows and peak outflows. Most of the discharge was between 100 and 1,000 L/d. About one-fourth of the time flow was less than 100 L/d, and this flow accounted for approximately 7 pct of the total output. In contrast, discharges over 1,000 L/d took place only about 4 pct of the time, but accounted for roughly one-third of the total output. Monthly flows were approximately equal from May to September, and reached a maximum of 13,700 L in October. The maximum vertical hydraulic loading on the bed was 5.7×10^{-3} cm/s, which occurred on 2 October. The saturated hydraulic conductivity at this flow, with an estimated ponding depth of 1.1 m, was 3.8×10^{-3} cm/s.

Influent trace metal concentrations, which peaked in September, were dominated by Ni, followed by Cu, Co, and Zn (table 14). Effluent trace metal concentrations and pH tended to parallel influent levels (fig. 12). The difference between effluent and influent levels was greatest at the beginning of the study period and subsequently decreased. The influent pH ranged from 6.3 to 7.15; effluent values were initially as high as 7.4 but dropped to as low as 6.5 by October. The effluent pH at the end of the period was even slightly lower than the influent pH.

The saturated bed removed approximately 20 mg CEU/kg of dry tailing in 1983, with removal generally decreasing over time. The mass of nickel removed by the bed was greater than that of the other three metals, but the percent of nickel removed was the lowest (table 15). Copper achieved the second highest mass removal and the greatest percent removal.

Discussion

The saturated bed received 44,000 L of leachate containing 73 g CEU of which 29 g, or 37 pct, was removed. Copper removal accounted for 19 g of CEU removal and nickel removal for 4.7 g. Although effluent copper concentrations increased at the end of the season, copper removal was fairly consistent, ranging from 85 to 95 pct. Removal of Ni, Co, and Zn tended to decrease over the study, suggesting the removal capacities for these metals were approached.

The CEU removal per unit mass tailings was about the same as that observed for the unsaturated bed (table 13). The values for the individual metals followed trends similar to those observed in

TABLE 14. - Influent and Effluent Flow and Chemical Data, Saturated Bed, 1983

Time period	Cumulative flow volume, bv[1]	pH	Concentration, mg/l				
			Cu	Ni	Co	Zn	CEU
			INFLUENT				
5/16- 6/ 2[2]	0.97	7.0	0.07	3.26	0.14	0.11	0.55
6/ 2- 6/17[2]	4.35	6.9	.07	4.87	.19	.10	.76
6/17- 6/24[3]	5.78	6.9	.09	5.93	.24	.11	.93
6/24- 7/ 1[3]	6.42	6.9	.07	4.87	.19	.10	.76
7/ 1- 7/ 8[3]	21.60	7.0	.20	5.71	.25	.15	1.04
7/ 8- 7/15[3]	23.15	6.9	.13	4.39	.19	.12	.77
7/15- 7/29[2,3]	23.66	6.9	.26	7.47	.28	.23	1.31
7/29- 8/ 4[3]	24.30	6.7	.23	4.20	.22	.21	.89
8/ 4- 8/12[3]	26.45	6.3	.52	8.32	.39	.34	1.78
8/12- 8/19[3]	27.85	6.4	.50	9.97	.45	.36	1.98
8/19- 8/26	34.52	6.75	.83	10.93	.47	.38	2.43
8/26- 9/ 1	37.88	6.85	.63	9.10	.40	.33	1.97
9/ 1- 9/ 8	38.92	6.8	.53	7.93	.35	.30	1.70
9/ 8- 9/16	41.72	6.75	.77	11.30	.50	.37	2.44
9/16- 9/22	43.01	6.7	.96	12.10	.50	.43	2.71
9/22- 9/30[2]	44.09	7.1	.78	10.22	.46	.35	2.30
9/30-10/ 5	53.96	6.85	.62	8.81	.37	.29	1.90
10/ 5-10/13	59.08	6.9	.52	8.12	.34	.26	1.70
10/13-10/20	63.12	7.15	.44	7.74	.31	.24	1.55
10/20-10/27	64.25	6.85	.39	7.20	.28	.24	1.41
			EFFLUENT				
5/16- 6/ 2	.98	7.4	<.01	.10	.01	.01	.03
6/ 2- 6/17	4.36	7.15	.01	.22	.02	.01	.05
6/17- 6/24	5.79	7.35	<.01	.55	.02	.01	.08
6/24- 7/ 8	21.63	7.0	.01	5.8	.18	.03	.77
7/ 8- 7/15	23.18	7.3	.02	3.49	.08	.02	.45
7/15- 8/ 4	24.33	7.2	.03	2.68	.06	.01	.36
8/ 4- 8/12	26.48	6.85	.01	1.80	.04	.01	.23
8/12- 8/19	27.88	6.95	<.01	3.60	.06	.01	.43
8/19- 8/26	34.55	6.9	.01	13.45	.46	.08	1.82
8/26- 9/ 1	37.91	7.0	.01	10.92	.38	.10	1.49
9/ 1- 9/ 8	38.95	7.15	.01	9.71	.29	.09	1.28
9/ 8- 9/14	41.33	6.9	<.01	7.51	.28	.09	1.04
9/14- 9/22	43.04	6.7	.01	11.92	.46	.22	1.68
9/22-10/ 5	54.00	6.6	.06	9.82	.40	.33	1.48
10/ 5-10/12	58.62	6.5	.05	6.43	.27	.23	.99
10/12-10/20	63.16	6.65	.04	6.67	.26	.20	.99
10/20-10/27	64.29	6.75	.05	8.89	.32	.23	1.28

[1] One bv = 679 L.

[2] Water quality data from monthly composite sample.

[3] Input data from FL-1 flow meter readings, except for 8/16 to 8/19; remaining input data from saturated bed flow meter readings.

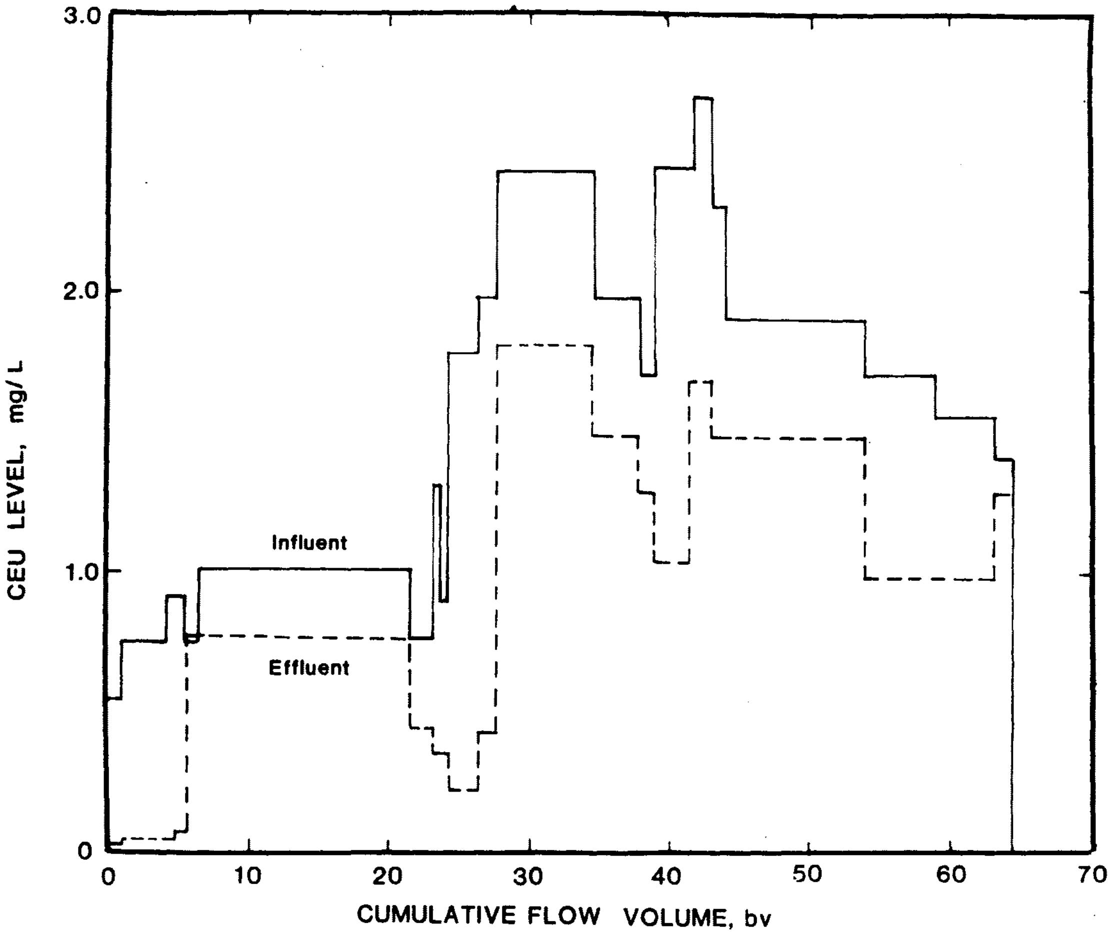


FIGURE 12.- Influent and effluent CEU level versus cumulative flow volume, saturated bed.

TABLE 15. - Metal Removal by Saturated Bed

Metal	Mass, g			Pct removal	Removal per mass of bed, mg/kg
	Input	Output	Removal		
Cu...	20	1.1	19	95	15
Ni...	340	310	30	9	23
Co...	15	11	4	27	3
Zn...	11	5.4	6	55	5
CEU...	70	44	26	37	20

the unsaturated bed. In both cases the mass removal of nickel was greatest followed by copper; cobalt and zinc removals were considerably lower. As was the case for the unsaturated bed, percent removal of copper was highest and that of nickel was lowest.

Copper removal by the saturated bed was greater than that by the unsaturated bed. This was most likely the result of differences in flow distribution. The majority of unsaturated bed flow occurred through the 29 pct of the bed nearest the input weir. Thus, the capacity of the tailings near the weir was depleted while that of tailings in more distant segments was relatively unused. In contrast, flow through the saturated bed contacted the tailings present more uniformly. Therefore the available capacity was used more efficiently.

Removal of nickel and cobalt by the unsaturated bed was greater than that by the saturated bed. This may have been the result of differences in leachate composition between 1982 and 1983. In the unsaturated bed, 81 pct of the nickel removal and 74 pct of the cobalt removal occurred in 1982. The median input pH during this period was 7.0 as compared to 6.85 in 1983. This decrease in pH may have contributed to the lower removal by the saturated bed. Also, in 1983 copper contributed 32 pct of the input CEU, as opposed to 16 pct in 1982. Copper removal was about 90 pct in both years, indicating a strong tendency for binding with adsorptive sites on the tailings. The elevated copper concentrations in 1983 would have tended to increase the potential for occupying adsorptive sites with copper. This, in turn, would have tended to decrease the removal of other trace metals such as nickel and cobalt.

The effluent CEU level was influenced by the influent CEU level, cumulative flow volume through the bed and flow rate. However, isolating the individual effects of these three variables was difficult. The influent composition, cumulative flow volume, and flow rate varied simultaneously. As the season progressed, the cumulative flow volume strictly increased and trace metal concentrations generally increased. Flow rates were also higher near the end of the season. Due to these continual variations it was difficult to determine the influence of a specific variable on effluent quality.

It is possible to determine correlations between effluent CEU levels and the three variable listed. Due to the aforementioned shortcomings, however, correlations must be interpreted with caution. The effect of the influent CEU level on the effluent CEU level was indicated by the similarities in their variation over the study (fig. 12). This influence is further illustrated by the correlation:

$$CEU_e = 0.67\ CEU_i - 0.22;\ r^2 = 0.55;\ n = 17, \qquad (9)$$

where CEU_e and CEU_i are the CEU levels of the effluent and influent, respectively. The observed correlation was largely due to variations in Ni, Co, and Zn concentrations since effluent Cu concentrations were relatively constant throughout the season. The degree of scatter in this figure and the anomalies illustrated in fig. 12 suggest that other variables also influence effluent quality.

To normalize for the effect of influent CEU levels, the effects of the other variables on the CEU reduction were examined. The CEU reduction appeared to decrease as the cumulative flow through the bed increased, although it fell below 24 pct only at the very end of the 1983 flow season (table 14). Almost all of the variation was due to reductions in concentrations of Ni, Co, and Zn since the reduction in Cu concentration was fairly constant throughout the season.

The pct CEU reduction was rather high, greater than 50 pct,during or immediately following periods of when discharge was below about 0.25 bv/d. This suggests that the extent of metal removal increased at lower flows, similar to the results obtained with tailings columns in the laboratory experiments.

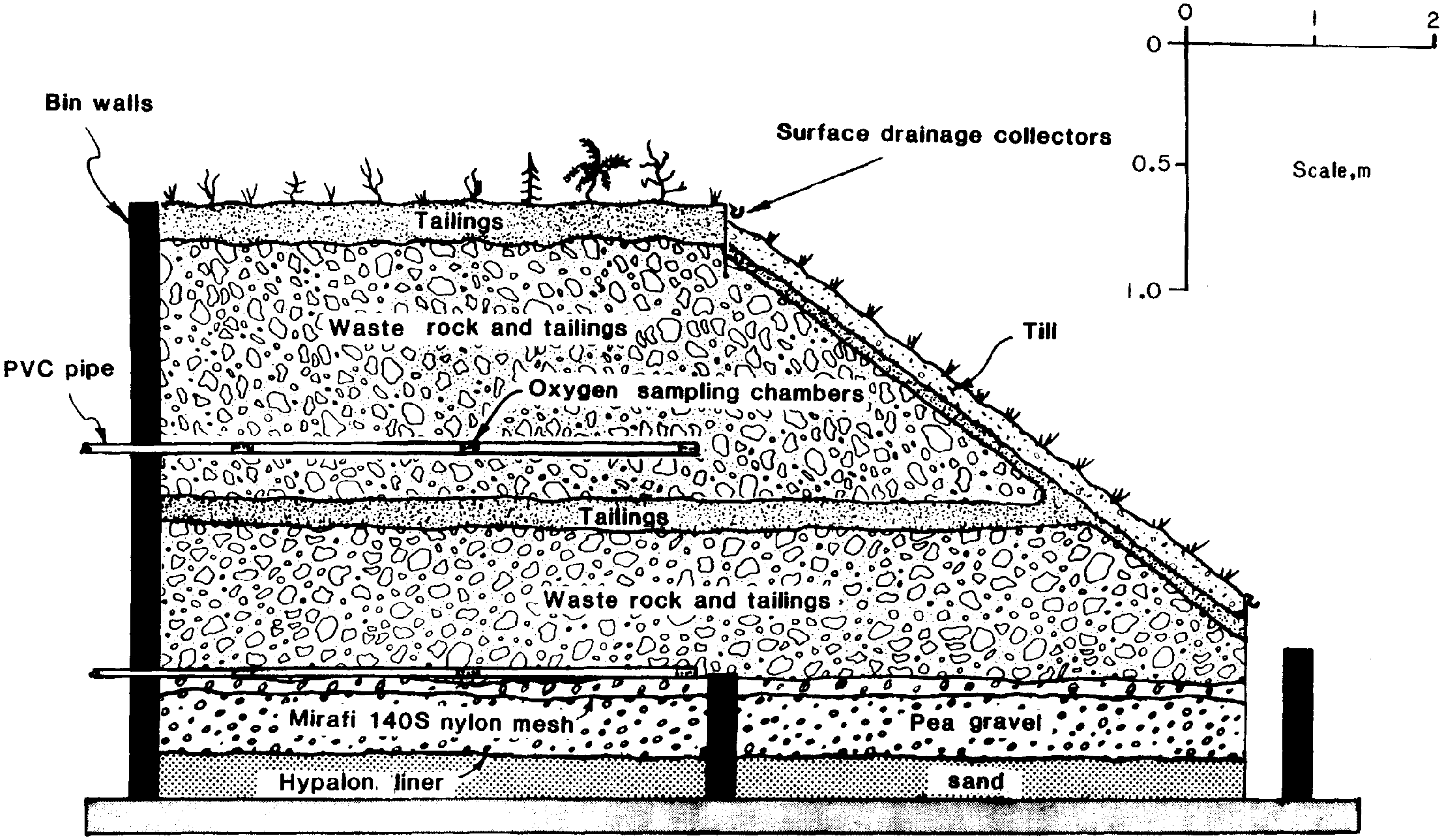
Joint Disposal Bins

Methods

Bin Construction

Six parallel bins were constructed at the test site near Babbitt, Minnesota. A pair of bins was allotted to each of three treatments: tailings mixed with waste rock, tailings mixed with waste rock with a vegetative cover over a tailings/soil root zone, and waste rock without tailings or vegetation (controls). The first treatment was designed to simulate treatment while piles are under construction. The cover and vegetation added in the second treatment would represent treatment for completed waste rock disposal areas.

Final bin design was determined by several criteria: 1) both the top and side slopes of a pile were to be simulated, 2) the minimum acceptable plot size for soil loss measurement was 1.5 m wide by 4.6 m long (136), 3) the minimum acceptable rooting depth was 15 cm (7); and 4) the mass of available tailings was limited. Each bin contained two sections, a relatively flat rear section to simulate the main portion of a waste rock pile and a front section which was sloped to simulate the side of a waste rock pile (fig. 13).



(Subsurface drainage system not shown)

FIGURE 13.- Cross-section of joint disposal bins 1 and 2.

The bins (1.5 m wide, 9.8 m long, 1.8 m high) were constructed of railroad ties set on a concrete slab, which was sloped toward the front at 2 pct. Waste rock from test stockpile FL-4 (fig. 1) was added in approximately 0.6-m lifts to bins one through four. Dry tailings were added in 10-cm layers to the top of each lift and water was used to distribute the tailings into the rock. Equal volumes of water were applied to control bins five and six for consistency. The surface of the rear section of the plots was relatively flat, sloped 50:1 (horizontal:vertical) toward the front. In contrast, the rock in the front section was loaded to form a 3:1 slope.

One piece of modified 10-cm PVC pipe was placed across the bottom of the relatively flat rear slopes, and one across the bottom of the front slopes to collect surface runoff separately from these sections. Each surface runoff collector drained through a 2.5-cm polyethylene hose to a 200-L barrel. The subsurface drainage collection system at the base of the bins consisted of 10-cm drain tile and 3.8-cm PVC pipe installed to collect flow separately from the rear and front sections. This collection system was covered with 20 cm of pea gravel, a layer of nylon mesh and then another 8 cm of gravel. A PVC pipe containing oxygen sampling equipment was placed above the upper gravel layer. An additional oxygen sampling device was installed at mid-level in each bin.

Initially 15 cm of tailings were applied as the cover material for both the flat and sloped segments of the vegetated bins. However, during rainfall simulation tests (54) severe erosion of the front slopes occurred and the tailings covers were lost. The slopes were then reconstructed with 10 cm of glacial till (loamy sand) over 5 cm of tailings. To determine the volume and quality of water percolating through the till but flowing along the top of the tailings layer, interflow collectors, consisting of 10-slot PVC wellscreen, were placed at the base of the till layer. These collectors drained to 19-L containers located in front of the bins.

In May 1983, the tailings and till covers in bins one and two were fertilized, seeded and mulched. The tailings layers on the rear sections of plots one and two were fertilized at a rate of 110 kg/ha N, 280 kg/ha P_2O_5 and 200 kg/ha K_2O, while the front slope till cover received a "standard" 10-10-10 fertilizer at a rate of 670 kg/ha. The seed mix, comprised of smooth bromegrass, reed canarygrass, timothy, perennial ryegrass, and birdsfoot trefoil, was applied at 45 kg/ha. These species had performed well in previous tailings vegetation research (8). After seeding, a straw mulch was applied at a rate of 5,000 kg/ha, and the beds were covered with plastic erosion-control netting. Both bins were watered immediately after seeding to promote germination. The equivalent of 1.25 and 2.5 cm of rainfall was applied to the front and rear plots, respectively. No additional watering was required until 9 August when, after a prolonged dry period, about 0.5 cm of water was applied to the front and rear of both bins.

Drainage Monitoring

Surface and subsurface discharge volume, water quality, and precipitation amounts were monitored throughout 1983. A cumulative flow meter and a Rustrak event recorder monitored the subsurface outflow from the base of the bins. The volume of surface runoff was measured for each rainfall event and water quality samples were collected whenever a precipitation event exceeded 1.3 cm. Flow-weighted composites were collected from the subsurface outflow using a 19-L plastic sump and a level-activated pump. Composite samples were collected monthly and for rain events exceeding 2.5 cm. For those bins covered with till and vegetated, the interflow between the till and underlying tailings was measured after each rainfall and water quality samples were collected for most storms with rainfall greater than 2.5 cm. Water quality analyses were conducted for suspended sediment, pH, Cu, Ni, Co, Zn, Ca, Mg, Na, SO_4 and total alkalinity.

Bin Oxygen Levels

Two sets of oxygen sampling devices were placed in each test bin, one at a depth of 0.95 m and the other at 1.9 m (fig. 13). The sampler design was similar to that used in a study of coal mine spoils (66). Each sampler contained three sampling chambers that were coupled to one another with PVC pipe. Samples were taken from the tubes with a hand pump attached to a measuring chamber. Stable oxygen levels were observed after eight volumes of the sampling system were pumped through the apparatus.

Vegetation Measurement

The vegetation on bins one and two was measured for percent cover and biomass on 26 August 1983, 3 months after seeding. Cover within a randomly placed hoop was estimated at four sites on each bin. Biomass was measured by the clip-and-weigh method (125). Half of the vegetation in each hoop was clipped, oven dried at 60^0 C for 24 h and weighed. A species list was also compiled and ranked according to biomass.

Results

Input

The three sources of input water for the joint disposal bins in 1983 were the snowmelt from the 1982/83 winter snowpack, rainfall and the water used to irrigate plots one and two. Snowpack measurements taken on 3 March indicated a rainfall equivalent of 8.0 to 11.0 cm on the front plots and 5.9 to 8.9 cm on the rear plots. The total precipitation, principally rainfall, at the study site from 31 March to 21 November was 55.1 cm. Of this total, 6.5 cm occurred before the 1 June start of monitoring the interflow from the cover layer on plots one and two. Precipitation from April through June was only 10.8 cm, approximately one-half of the average rainfall for this period. Seventy three percent of the total precipitation (40.4 cm) fell between the beginning of July and the end of October. As previously mentioned, plots one and two were watered twice, on 27 May and 9 August, to encourage the vegetative growth.

Periodic pH and specific conductance measurements of 1983 rainfall showed ranges of 3.65 to 5.2 and 13 to 45 uS/cm, respectively. No chemical data were available for the snowpack or the irrigation water. The latter was supplied by a Kennecott well in a bedrock aquifer. Bedrock wells in the study area generally have a pH of 7.0 to 9.0 and conductivity readings one to two orders of magnitude above those mentioned above for the rainfall (114).

Vegetation Measurement

The percent cover and biomass were slightly greater on the flat rear tailings portion of plots one and two than on the front slope till. The flat portion averaged 84 pct live cover and 1,980 kg/ha biomass, while the front slope averaged 62 pct cover and 1,490 kg/ha biomass. Perennial ryegrass and smooth bromegrass, along with volunteer oats from the mulch, were the dominant species. Other volunteers included lambsquarter and red and alsike clover.

Physical Data

The input to each bin was approximately 8,500 L (63 cm of rainfall), and total outputs ranged from 1,700 to 6,200 L. The average total drainage volume for the vegetated, unvegetated, and control bins were respectively, 23, 45, and 68 pct of the precipitation input (table 16). Subsurface output contributed the largest fraction of the total drainage from all bins, ranging from 17 to 68 pct of the total precipitation input. Essentially all drainage from the control bins occurred as subsurface drainage, and it exceeded that from the vegetated and unvegetated bins by factors of four and two, respectively.

Surface runoff averaged 420 L for the vegetated bins and 990 L for the unvegetated bins containing tailings, representing only 5 and 12 pct, respectively, of the rainfall on the bins. Virtually all surface runoff from the unvegetated bins was from the front slope. The surface runoff values from the vegetated bins were in close agreement, but those from the unvegetated tailings bins differed by almost a factor of two, possibly due to differences in the distribution of tailings on the surface. The

TABLE 16. - Distribution of Flow Output from Joint Disposal Bins, 1983

Bin	Average value as pct of total input[1]						
	Surface		Subsurface		Interflow[2]	Total drainage	[3]ET+ Δ S
	Front	Back	Front	Back			
1, 2..	2.8	2.2	12	5.0	0.52	23	77
3, 4..	11.5	[4]0.18	16	17	NAp	45	55
5, 6..	[4]0.4	[4].18	32	36	NAp	69	31

NAp not applicable.

[1] Flow distribution values for each pair of bins were reasonably consistent.

[2] Interflow from cover material.

[3] Evapotranspiration plus change in storage.

[4] Virtually all direct rainfall into surface runoff collectors.

combined surface runoff from the unvegetated bins was twice that from the vegetated bins, but for both treatments was about 25 pct of the total drainage. Some surface runoff was recorded from the control bins and the flat segment of the unvegetated tailings bins, but it was less than 1 pct of the total rainfall. Based on field observations and previous rainfall simulation studies, it was largely due to direct precipitation into the collection gutters. A small amount of interflow was also collected from the cover layer of the vegetated bins, but for both bins it was less than 1 pct of the total rainfall.

The total drainage was fairly evenly divided between the sloped (front) and flat (rear) sections of the control bins. In the remaining bins discharge from the sloped sections of the bins was 1.4 to 2 times that from the rear. Surface runoff from the vegetated bins was fairly evenly divided between the sections, but subsurface discharge from the sloped section was 2.5 times that from the flat section. In the unvegetated tailings bins the subsurface output was evenly distributed, and the surface runoff volume accounted for the difference (table 16).

Soil losses followed a pattern similar to surface runoff. Losses from the control bins and the flat segments of the unvegetated tailings bins were low compared to those from the other bins (table 17). Soil losses from the front slopes of the unvegetated tailings bins were 10 to 60 times those from the slopes of the vegetated bins. Average TSS (total suspended solids) levels from all types of bins were elevated, but were highest from the unvegetated tailings surfaces and lowest from the controls (table 17).

Chemical Data

The flow-weighted mean CEU levels in subsurface output from the sloped segment of the bins ranged from 0.25 to 0.54 mg/L, of which 40 to 60 pct (0.15 to 0.36 mg/L) was contributed by nickel (table 18). Although the lowest level was from one of the unvegetated tailings bins, there was considerable variation within all three pairs of bins. CEU levels in subsurface drainage from the flat segments of both types of treated bins were in the range of 0.22 to 0.34 mg/L, while higher values (0.54 to 1.62 mg/L) were observed for the controls. The variation in the CEU levels between control bins probably resulted from variations in the sulfide content and/or particle size of the waste rock placed in the bins. Median pH values for subsurface drainage from the treated piles were 0.6 to 1.2 units higher than the controls.

As previously mentioned, appreciable surface runoff occurred only from the vegetated bins and the sloped section of the unvegetated tailings bins. In the vegetated bins the CEU levels in surface runoff were less than 10 pct of those in the subsurface drainage (table 18). CEU levels in surface runoff from the

TABLE 17. - Solids Loss and Mean TSS in Surface Runoff from Joint Disposal Bins, 1983

Bin	7 March to 21 Nov.				1 June to 21 Nov. (Period after revegetation)			
	Front		Back		Front		Back	
	Solids loss, mt/ha	Flow-weighted mean TSS, mg/L	Solids loss, mt/ha	Flow-weighted mean TSS, mg/L	Solids loss, mt/ha	Flow-weighted mean TSS, mg/L	Solids loss, mt/ha	Flow-weighted mean TSS, mg/L
1....	21	63,000	0.14	560	0.87	2,750	0.14	570
2....	13	30,000	0.22	730	0.40	1,120	0.22	740
3....	24	11,600	0.0070	190	23	12,000	0.0070	210
4....	12	10,000	0.0030	300	10	9,750	0.0030	290
5....	0.0043	400	0.0027	150	0.0043	720	0.0027	210
6....	0.011	110	0.0030	110	0.011	130	0.0030	120

TABLE 18. - Flow Weighted Mean Concentrations from Joint Disposal Bins, 1983

Bin	Outflow	Front Slope Segment								Back Segment							
		Flow Output, L	Median pH	Flow weighted mean concentration, mg/L						Flow Output, L	Median pH	Flow weighted mean concentration, mg/L					
				Cu	Ni	Co	Zn	CEU	SO_4			Cu	Ni	Co	Zn	CEU	SO_4
1	Surface...	200	6.0	0.008	0.022	0.006	0.016	0.018	22	170	5.8	0.013	0.006	0.006	0.033	0.023	39
	Subsurface..	880	7.4	.098	3.57	.069	.18	.54	2,300	350	7.8	.068	1.00	.048	.073	.22	2,900
	Interflow[1]..	45	5.0	.013	.06	.027	.10	.056	440	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp
2	Surface...	270	5.7	.009	.007	.007	.022	.020	21	200	5.8	.010	.006	.006	.033	.023	29
	Subsurface..	1,200	7.5	.064	2.03	.055	.31	.35	2,300	490	7.8	.074	1.97	.062	.043	.34	2,800
	Interflow[1]..	43	5.2	.001	.063	.023	.11	.053	420	NAp	NAp	NAp	NAp	NAp	NAp	NAp	NAp
3	Surface...	1,250	6.2	.038	.33	.027	.028	.10	380	25	4.6	.012	.008	.008	.024	.023	20
	Subsurface..	1,280	7.5	.11	2.27	.057	.12	.41	1,900	1,370	7.8	.038	1.34	.045	.028	.22	2,300
4	Surface...	690	6.0	.61	3.17	.17	.12	1.11	380	7	5.9	.03	0	0	.03	.03	30
	Subsurface..	1,460	7.6	.048	1.46	.041	.12	.25	1,400	1,500	7.4	.060	1.65	.055	.041	.28	1,900
5	Surface...	7	5.3	0	0	0	0	0	14	12	4.8	.017	.017	0	.033	.022	17
	Subsurface..	2,400	6.7	.17	1.90	.071	.15	.44	880	3,000	6.8	.19	2.67	.075	.15	.54	1,300
6	Surface...	62	4.7	.015	.015	.005	.023	.023	19	19	4.9	.01	.01	.01	.02	.024	21
	Subsurface..	3,100	6.6	.21	1.82	.070	.23	.48	750	3,070	6.8	.69	6.48	.24	.38	1.62	1,400

NAp Not applicable.

[1] From cover material.

unvegetated bins were 5 and 55 times higher than those from the vegetated bins, and in one bin were four times subsurface levels. The median pH of the surface runoff was at least 1.3 units lower than that of subsurface drainage in all cases.

The flow-weighted mean sulfate concentration in subsurface flow was lowest in the control bins and highest in the vegetated bins. In all cases, concentrations from the flat segment of the bin were higher than those from the sloped segment; 25 pct higher for the treated bins and 50 to 90 pct for the controls. Sulfate concentrations in surface runoff were generally less than 20 mg/L, except for runoff from the front slopes of the unvegetated tailings bins, where the median concentration was 380 mg/L.

Gas samples were collected for oxygen content measurement with respect to four variables: distance from back to front of bin, depth, type of bin, and time. The oxygen levels varied little with respect to the first two variables; the largest differences in oxygen levels were due to sampling date, while some variability with respect to the type of bin also occurred. In general, gases in the waste rock bins had the highest oxygen levels, followed by the waste rock/tailings bins with no cover and then by the vegetated waste rock/tailings bins. The observed levels do not indicate a great reduction in oxygen levels by the two treatments.

Chemical Mass Release

The trace metal release from the vegetated tailings bins was about 0.6 g CEU (table 19). Releases from the unvegetated tailings bins and the control bins were two and eight times higher, respectively. With one exception, 85 to 100 pct of the trace metal release was associated with subsurface flow. In bin 4 release was equally divided between surface and subsurface flows. Release associated with interflow from the cover layer of the vegetated bins was less than 1 pct of the total release from the bins. With the four bins containing tailings, 68 to 85 pct of the release was from the front of the bins while, for the control bins, the majority of release was from the back. The combined release from the back of the control bins was 25 times that from the back of the vegetated bins. For the front section, release from the controls was less than three times that from the vegetated bins.

Total sulfate mass release was lowest from the vegetated bins and highest from the controls. Virtually all sulfate release occurred with subsurface flow, although 5 to 10 pct of release from the unvegetated tailings bins was associated with surface runoff from the front of the bins. In the vegetated bins sulfate release from the front section was almost twice that from the back, while the opposite was observed for the controls. Subsurface release from the back of the unvegetated bins was about 30 pct higher than that from the front.

TABLE 19. - Mass Release from Joint Disposal Bins, 1983

Bin	Outflow	Front Slope							Back Segment						
		Flow Output, L	Mass release, g						Flow Output, L	Mass release, g					
			Cu	Ni	Co	Zn	CEU	SO_4		Cu	Ni	Co	Zn	CEU	SO_4
1	Surface.....	200	0.0016	0.0045	0.0012	0.0033	0.0036	4.5	170	0.002	0.0011	0.0011	0.0056	0.0038	6.7
	Subsurface..	880	.086	3.15	.061	.16	.48	2,000	350	.024	.36	.017	.026	.079	1,040
	Interflow[1]..	45	.0006	.0027	.0012	.0046	.0025	20	NAp	NAp	NAp	NAp	NAp	NAp	NAp
	Total.......	1,220	.088	3.15	.062	.16	.48	2,000	520	.028	.36	.020	.038	.087	1,070
2	Surface.....	270	.0025	.0018	.0019	.0058	.0052	5.6	200	.0026	.0012	.0012	.0065	.0046	5.7
2	Subsurface..	1,200	.077	2.45	.066	.37	.42	2,750	490	.036	.96	.030	.021	.16	1,370
2	Interflow[1]..	43	.0006	.0027	.0010	.0047	.0023	18	NAp	NAp	NAp	NAp	NAp	NAp	NAp
2	Total.......	1,510	.080	2.45	.068	.37	.43	2,760	690	.039	.96	.032	.032	.17	1,390
3	Surface.....	1,250	.048	.42	.034	.035	.13	471	25	.0003	.0002	.0002	.0006	.00058	.5
3	Subsurface..	1,280	.146	2.90	.073	.16	.52	2,470	1,370	.052	1.83	.061	.038	.30	3,090
3	Total.......	2,530	.194	3.32	.11	.19	.65	2,940	1,390	.052	1.83	.061	.039	.30	3,090
4	Surface.....	690	.42	2.19	.12	.084	.77	265	7	.0002	0	0	.0002	.00022	.2
4	Subsurface..	1,460	.070	2.14	.060	.180	.36	2,080	1,500	.090	2.48	.083	.062	.43	2,810
4	Total.......	2,150	.49	4.33	.18	.26	1.13	2,340	1,510	.090	2.48	.083	.062	.43	2,810
5	Surface.....	7	0	0	0	0	0	0	12	.0002	.0002	0	.0004	.00076	.2
5	Subsurface..	2,400	.40	4.56	.17	.37	1.07	2,110	3,000	.56	8.01	.23	.45	1.63	4,020
5	Total.......	2,410	.40	4.56	.17	.37	1.07	2,110	3,010	.56	8.01	.23	.45	1.63	4,020
6	Surface.....	60	.0009	.0009	.0003	.0014	.0014	1.2	19	.0002	.0002	.0002	.0004	.00046	.4
6	Subsurface..	3,100	.640	5.63	.22	.72	1.49	2,320	3,070	2.13	19.9	.73	1.2	4.96	4,350
6	Total.......	3,160	.64	5.63	.22	.72	1.49	2,320	3,090	2.13	19.9	.73	1.2	4.96	4,350

NAp Not applicable.

[1] From cover material.

Discussion

The overall goal of the mixed disposal of tailings and waste rock strategy was reduction of the trace metal release from waste rock stockpiles. This release is the result of the oxidation of sulfide minerals and the subsequent transport of reaction products from the oxidation site. Mixing tailings with the waste rock offers potential to reduce trace metal release by: 1) promoting surface runoff which reduces water available for transporting oxidation products; 2) establishing vegetation thereby increasing transpiration and further reducing water available for transporting reaction products; 3) providing tailings within the waste rock to adsorb trace metals that are released within the pile; and 4) reducing sulfide oxidation by limiting oxygen access. It is evident from the results previously described that mixing tailings with waste rock has reduced metal release.

All of the trace metal release from the control bins occurred with subsurface flow, which represented 68 pct of the total input and was divided fairly evenly between the front (beneath the slope) and back beneath the flat segment) of the bins. However, trace metal concentrations were higher from the back of the bins, therefore the majority of trace metal release occurred from this section. These bins generated no surface runoff in the simulated rainfall studies, during which the application rate, 2×10^{-3} cm/s, exceeded that of the 100-yr storm. This indicated a steady-state infiltrability of at least 2×10^{-3} cm/s, and no surface runoff would be expected for storms of lesser intensity.

Promoting surface runoff was partially successful, with surface runoff from the treated bins ranging from 5 to 12 pct of the total rainfall on each bin. During significant rainfall events throughout the summer, surface runoff occurred on the front slopes of all treated bins and from the flat segments of the vegetated bins. Design modifications may increase runoff, particularly from the flat segments of the unvegetated bins.

During the rainfall simulation tests, water ponded on the flat segment of the unvegetated tailings, but no surface runoff was generated. This was due to the lack of a continuous layer of tailings and the small slope (50:1). Increasing the slope and/or tailings application would tend to increase surface runoff from the flat segment, and further reduce subsurface flow.

Enhancing the surface runoff from the unvegetated surface on the front slope could, however, involve a trade-off with water quality. The trace metal concentrations in this runoff were elevated and extensive erosion occurred. The flow-weighted mean CEU level in the surface runoff from the front slope of bin 3 was 0.1 mg/L, similar to levels observed in the rainfall simulation tests. Nickel concentrations correlated with suspended solids concentrations in the rainfall simulation tests ($r^2 = 0.87$) and in subsequent laboratory tests. Apparently reaction products were washed from the tailings, which had been stored in a sheltered bin for about 5 years (15).

The corresponding CEU levels from bin 4 were an order of magnitude higher than those from bin 3, and were higher than all subsurface levels except those from bin 6. There did not seem to be sufficient contact between the surface flow and waste rock to produce such elevated levels. Some interflow, with elevated trace metal concentrations, may have discharged on the front slope and contributed to the overland flow. Such interflow would be associated with a relatively impermeable layer within the stockpiled rock. Additional field observations will be made to determine the likelihood of interflow discharge on the front slope.

Severe erosion was also associated with surface runoff from the front slopes of bins 3 and 4. The tailings losses were estimated as 97 and 300 mt/ha. Despite such losses, enough tailings remained to reduce infiltration and enhance surface runoff. A smaller initial tailings application may have reduced infiltration without producing excessive solids loss from the slope.

Although surface runoff was generated from both the front slopes and back of the vegetated bins, the total volume was only 5 pct of the total input. This was less than half that generated from the front of the unvegetated bins, suggesting that the till, a loamy sand (table 1), had a higher infiltration capacity than the tailings/rock mixture. Estimating the surface infiltration as the difference between precipitation and surface runoff, the average infiltration rate of the vegetated bins was 24 pct higher than that of the unvegetated bins.

Many factors affect the infiltration rate including soil moisture, structure, texture, and uniformity. In the limiting case of continuous rainfall, the infiltration rate approaches the saturated hydraulic conductivity. Permeameter tests indicated that the saturated hydraulic conductivity for the loosely packed till (1.33 g/cm^3) was about 20 pct higher than that of the tailings packed at 1.55 g/cm^3 (table 4). The similarity of this ratio and that of the infiltration rates may be coincidental. As previously mentioned, the infiltration rates may be coincidental. In addition, the establishment of vegetation on the till would tend to increase the infiltration capacity (25). Similarly, the tailings/waste rock mixture would tend to have a higher permeability than the tailings alone.

The vegetation reduced erosion and trace metal concentrations in surface runoff. Trace metal concentrations were 2 to 20 pct of those in surface runoff from the unvegetated bins. The CEU levels in the surface runoff were low in comparison with other outputs, but exceeded regional background levels by an order of magnitude. Some of the trace metals were apparently contributed by contamination from the collection system rather than from soil-water contact. The CEU levels were comparable to those of bins in which the large majority of surface flow was generated by direct precipitation into the collection gutters. The erosion per bin was about five pct of that from the unvegetated bins. The average soil losses from the front and back of these bins were 0.54 and 0.18 mt/ha, respectively. These values are below the tolerable soil loss guideline of 13.6 mt/ha used by the Soil Conservation Service for agricultural soils (136).

In addition to promoting surface runoff, the total flow output was reduced 33 pct by the unvegetated tailings and 67 pct by the vegetated tailings. The first value is similar to the reduction observed for soil cover on larger test piles (31). The major reduction in drainage was the result of increased storage and evaporation, the sum of which equalled the difference between inputs and outputs (table 16). The increase in storage can be attributed to the addition of tailings. The incorporation of fine particles tends to increase the water retention capacity, and therefore storage, of the piled rock (57). For the tailings, a field capacity of 28 pct moisture on a mass basis was determined based on moisture retention measurements at 0.1 and 15 bars. Water retained near the surface would be more readily available for evaporation and transpiration, thus enhancing these outputs.

The total drainage from the vegetated tailings bins was half that of the unvegetated bins, suggesting that transpiration contributed to the reduction. The average biomass on the vegetated plots was 1.75 mt/ha. Evapotranspiration for grain plus straw at this density was in the range of 15 to 30 cm, when water supply limited both evaporation and photosynthesis (17). This represents a range of 2,000 to 4,000 L of outflow from each vegetated bin.

The amount of interflow in the cover material was small, about 0.5 pct of the total input. The subsurface drainage through the waste rock could be reduced further by compacting the tailings layer beneath the till. This would reduce the permeability of the tailings layer and generate a larger volume of interflow from the cover material. Since CEU levels in the interflow were only 10 to 15 pct of subsurface levels, trace metal release would be reduced if outflow occurred as interflow rather than subsurface drainage.

Not only did the treatments reduce infiltration, but the tailings also affected drainage chemistry. Although a thorough mixing of tailings and waste rock was impossible, the tailings nevertheless effectively reduced metal concentrations in the subsurface drainage. The reduction in the front of the bins was slight, while the reduction in the back was about 75 pct (table 19). The reduction was produced by both buffering the pH and adsorbing trace metals released by the waste rock. The pH of outflow from both the front and the back was about 0.8 units higher than the controls. Similar buffering effects were observed in the laboratory experiments, and previous field studies indicated that trace metal release from the stockpiles decreased as pH increased (31). The tailings also provided additional surface area for adsorption. In the laboratory experiments, trace metal removal increased with increasing pH, further emphasizing the role of pH in limiting trace metal release. Since no attempt was made to optimize the mixing of tailings with the waste rock, more detailed studies are necessary to quantify the reduction in trace metal release as a function of tailings placement and the tailings/ waste rock ratio.

There was no evidence that tailing addition lowered the sulfide oxidation rate by limiting oxygen access (6, 49, 72, 100). The oxygen levels in the treated bins were slightly lower than those in the controls. However, given the large variation of oxygen levels among sampling periods, it was not possible to conclude that the tailings had restricted oxygen transport into the bins. Sulfate release rate is one potential indicator of the rate of sulfide oxidation within a rock pile. Tailings addition did not affect the total sulfate release from the front of the bins, but it reduced release from the back by 30 pct. This reduction was due to a reduction in flow volume, since sulfate concentrations from the treated bins exceeded those from the controls. Sulfate concentrations decreased with increasing flow, as is the case for drainage from full-scale stockpiles (26, 27, 50). Thus, there is presently no evidence that tailings addition reduced the sulfide oxidation rate. It is possible that additional time is required for the treatment to influence oxygen transport and, consequently, sulfide oxidation rates.

In summary, the mixed disposal of tailings and waste rock successfully reduced the concentration and total mass release of trace metals in drainage water. When compared to the controls, vegetated tailings bins had 66 pct less flow output, 60 pct lower CEU levels, and 87 pct lower CEU mass release. The reductions in unvegetated bins were 33 pct less flow output, 56 pct lower CEU levels, and 72 pct less mass release than the control bins. The treatments reduced the percolation of precipitation through the waste rock by increasing storage, evaporation, transpiration (in vegetated bins), and surface runoff. The tailings reduced trace metal concentration and raised the pH, but no decrease in the rate of sulfide oxidation was observed.

The two major drawbacks of the unvegetated tailings treatment were elevated trace metal concentrations and erosion associated with the surface runoff. These drawbacks were eliminated when vegetation was established on the surface. The vegetation also reduced total drainage by providing a transpiration component, but did not influence the sulfide oxidation rate.

The treatment strategy improved drainage quality under the given test conditions, but trace metal concentrations were still above those found in local surface water. The method's applicability for any actual mining operation will, therefore, depend on site specific geology and hydrology as well as on the water quality standards applied to the site.

EFFLUENT GUIDELINES

Effluent guidelines were needed to determine if effective water treatment was achieved. That is, the treatment techniques improved drainage water quality, but how did drainage quality compare with effluent guidelines? The guidelines used for this comparison were technology-based, or performance standards, supplemented by data on relative trace metal toxicities. More stringent limitations could be mandated to protect receiving water quality.

The guidelines were determined as follows:

1) The EPA New Source Performance Standards (NSPS) effluent limitations for copper mine drainage, average daily values for 30 consecutive days (40 CFR 440.104) were used (the NSPS for nickel mine drainage have not yet been promulgated). These standards include 0.15 mg/l copper, 0.75 mg/l zinc, 20.0 mg/l TSS and pH in the range 6.0 to 9.0.

2) The EPA development document for the ore mining and dressing NSPS (126) did not examine cobalt and excluded nickel from the effluent limitations, stating "the limitations on copper, lead, zinc and mercury would ensure adequate control of nickel"; however, the fact that the EPA study examined only one nickel mine (in a lateritic ore in Oregon) along with the results of the present study, does not seem to justify the exclusion for nickel.

3) Bioassay studies indicated that the relative toxicities of copper and cobalt were roughly equal, as were those of nickel and zinc (67); these results were used to justify setting the nickel guideline equal to that of zinc, 0.75 mg/l, and the cobalt guideline equal to that of copper, 0.15 mg/l; the Canadian Federal Metal Mining Liquid Effluent Regulations (S.O.R./77-178), which are technology-based, have also set limitations for nickel equal to those of zinc.

FIELD APPLICATIONS

Introduction

Numerous options exist for using low sulfur tailings to remove trace metals from mine drainage of near-neutral pH. These options may provide low- cost treatment for part or all of the mining runoff from a given mining operation. Prior to implementation in an actual operation, large scale field testing of a given treatment system would be required. Some preliminary designs are presented below as potential candidates for such testing. These designs are largely conceptual but do include rough estimates of the system size and tailings mass requirements.

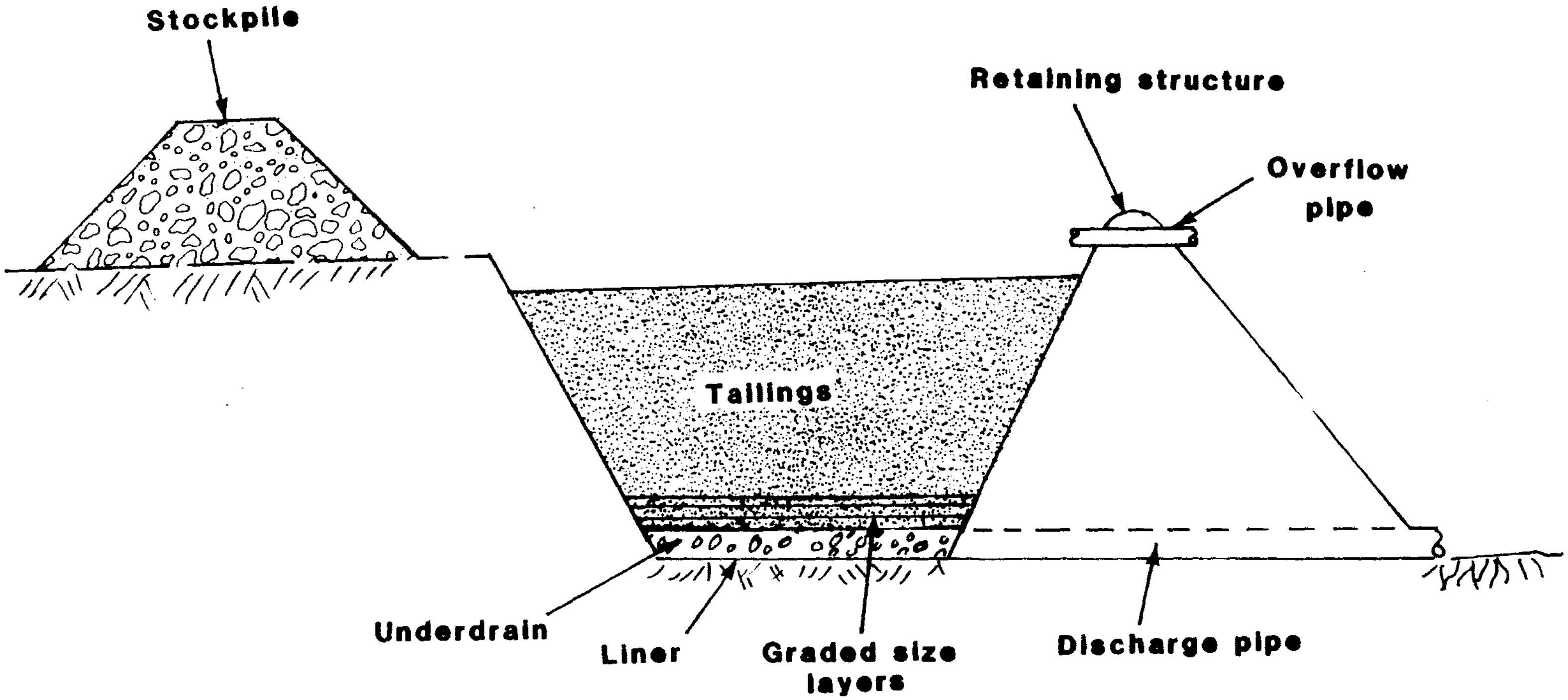
Tailings Treatment Beds

In a mining operation, treatment bed construction would be similar to that in the field tests. A permeable layer, or underdrain, below the tailings would be required to transmit discharge from the bed. This layer would consist of particles much larger than the tailings such as the pea rock used in the field tests. A layer of mesh, as was used in the field tests, or layers of selected particle sizes between the tailings and the underdrain (44, 116) would be required to prohibit migration of tailings into the underdrain system.

Drainage would flow from stockpiles, through an input distribution system (a weir for example), through the tailings, the graded layer, and the underdrain. Several underdrain configurations involving pipe and/or blanket drains are possible (44). A retaining structure would be necessary to contain the tailings, and pipe or drain tile would transmit flow through this structure (figs. 14, 15). After passing through the retaining structure, flow would be discharged to the environment.

In a passive system, flow would occur by gravity as opposed to pumping. This imposes constraints on the relative elevations of components within the system. The topography of the area may determine these elevations and may, therefore, be the major factor in hydraulic design. The difference in elevation between the stockpile base and the point of discharge from the bed must be adequate to account for the depth of the system components and the associated head losses. For either an unsaturated or saturated bed, the point of stockpile drainage must be above the surface of the treatment bed. The elevation difference would be determined by the head losses in the flow collection and input flow distribution systems, and the freeboard height above the tailings. The freeboard required for an unsaturated bed would be less than that required for a saturated bed. The amount of local relief needed for a passive system to function would be less for a saturated than an unsaturated bed, due to the relative elevation of the discharge outlet (figs. 14, 15).

A number of hydraulic considerations will determine the mass of tailings and the area required for treatment beds. Among these are the hydraulic conductivity of the bed, the height of the bed, the head differential between the water level and the bed discharge outlet, the magnitude and duration of maximum flow events, provisions for surface storage of peak flow runoff, and whether the flow system is saturated or unsaturated. For a



Not to Scale

FIGURE 14.- Schematic of operational scale tailings treatment bed, unsaturated flow.

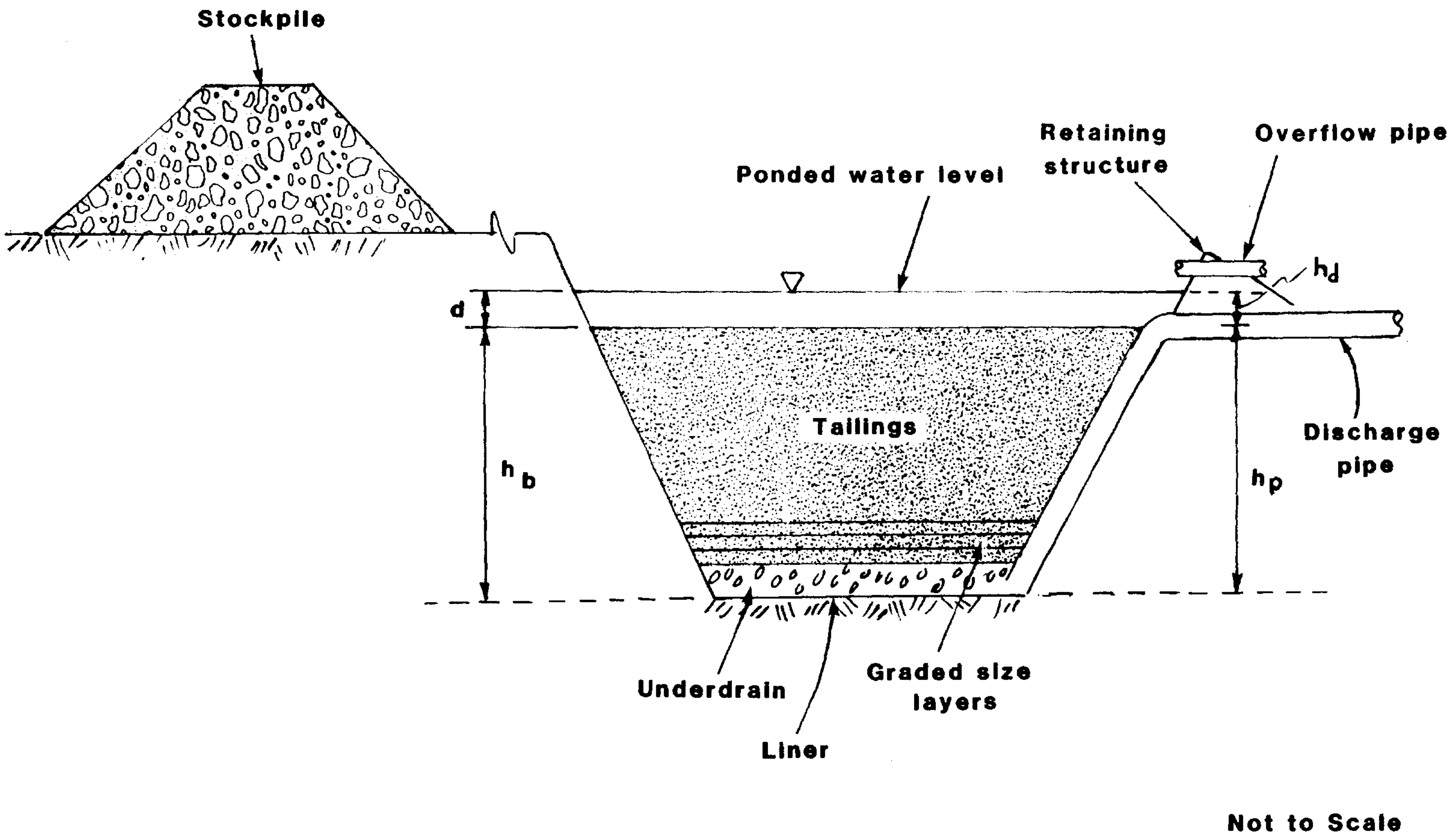


FIGURE 15.- Schematic of operational scale tailings treatment bed, saturated flow.

saturated flow treatment bed similar to that shown in figure 15, bed hydraulic capacity would be governed by the relation (79):

$$M = dCA_s ph_b/(tK_s h_d/h_b - p) \qquad (10)$$

where M = mass of tailings in treatment bed (m),
p = design storm rainfall depth (m),
C = runoff coefficient (dimensionless),
A_s = stockpile area (m^2),
d = bulk density of tailings in treatment bed (mt/m^3),
h_b = depth of bed (m),
t = time of rainfall (s),
K_s = saturated hydraulic conductivity (m/s), and
h_d = height difference between ponded water level and discharge pipe level (m).

This relation assumes: A) no groundwater seepage; B) no change in surface storage; C) the sole inputs are direct precipitation and stockpile drainage; D) input to the bed from these two inputs occurs simultaneously; E) both inflows are at a constant rate; and F) the duration of bed outflow equals that of the inflow.

Hydraulic conductivity is a particularly important variable because it may vary over several orders of magnitude. In order for a full-scale treatment bed such as that presented in figure 15 to be suitable from a hydraulic standpoint, it would require a minimum conductivity of approximately 10^{-3} cm/sec. Bed conductivity values greater than 10^{-3} cm/sec might be achieved by removing some finer tailings fractions before construction, but this could also decrease the effectiveness of contaminant removal.

Joint Disposal

Design considerations applicable to full scale joint disposal include stockpile area height and slope angles, and tailings stabilization. Unstabilized tailings, even on the relatively flat bed portion of the joint disposal bins, eroded during the rainulator tests. Extensive flat areas of unstabilized tailing would also be susceptible to wind erosion (23). Possible stabilization methods could include early establishment of vegetation, construction of wind breaks, use of chemical binders, or covering with till. Alternate capping methods, perhaps involving several layers, with bentonite-modified soils, geomembrane and/or coarse drains (96) might be possible, although more expensive than tailings stabilization.

The placement of tailings in relation to the waste rock must also be considered. Methods to achieve an optimum mixture of tailings and waste rock should be investigated. Tailings could be spigoted onto the pile, or dry tailings could be hauled by truck. Proposals for the Crandon Mine Project in Wisconsin include placing a layer of tailings beneath waste rock embankments (38), which could provide a bed for treatment of stockpile drainage.

The incorporation of tailings with waste rock would reduce the area required for overall waste disposal. Mine models predict a tailings:waste rock mass ratio of 1 to 3 (130). The approximately 1:5 mass ratio examined in the present study would account for the disposal of at least 20 pct of the tailings produced in a full scale operation.

General Considerations

The use of low sulfide tailings as a method of passive treatment for mine drainage does have several drawbacks. Most of these, however, are problems that would ordinarily be encountered in tailings disposal. The erosion of tailings by both wind and water from the surface of treatment beds or joint disposal caps must be controlled, such as by improvement with till and/or revegetation. For joint disposal treatment effluent, it may be necessary to construct a toe ditch and berm, a settling basin, or a similar structure to minimize TSS levels.

Seepage through the underdrain liner of a treatment system (figs. 13, 14, 15) could affect groundwater quality. The type of underdrain system and the liner material chosen are the principal factors in controlling seepage (90). Options for liner materials include synthetic membranes, bentonite-modified till and native clay (38, 43). Synthetic liners are typically quite expensive. In using naturally occurring materials such as till or clay, their local availability becomes a principal consideration.

The low sulfur copper-nickel tailings retain some of the same metal sulfide minerals that are susceptible to oxidation and leaching in the waste rock. The tailings used in this study contained 0.095 to 0.38 pct sulfur, which is almost identical to the 0.1 to 0.35 pct range reported in beneficiation studies on Duluth Complex ore (61, 109). As indicated in the present study and in previous laboratory experiments, these low sulfur tailings are not acid producers and have a very low rate of trace metal release (61, 78). The question of what may happen with the long-term environmental exposure of low sulfur copper-nickel tailings remains unanswered. The release of trace metals from tailings under long-term conditions will be a function of tailings mineralogy and particle size distribution, as well as environmental conditions such as the degree and frequency of moisture saturation.

One of the most important factors affecting trace metal release is the presence of acid conditions. Some limited deposits of semi-massive sulfide ore exist in the Duluth Complex, and may produce tailings with enough residual iron sulfides (pyrrhotite, pyrite, troilite, mackinawite) to generate acid conditions. Leaching experiments suggest that a critical sulfur concentration in the tailings occurs between 0.92 and 2.65 pct sulfur (61). Tailings containing more than this critical percentage will produce acid. As conditions become more acidic, the trace metal removal efficiency of the tailings decreases, and the rate of trace metal release from tailings increases (78). The problems posed by high sulfur tailings could be eliminated by segregating high sulfur tailings for separate disposal by blending these tailings with those having a low residual sulfur content, or by removing the iron sulfides in the beneficiation process (107).

SUMMARY AND CONCLUSIONS

Laboratory batch and column studies indicated that peat, till and low sulfur copper-nickel tailings can remove dissolved trace metals from copper-nickel mine stockpile drainage in the neutral pH range. The low cost and availability of peat, till and tailings in northeastern Minnesota make them attractive for passive treatment schemes, despite their rather low metal removal capacities. Tailings are particularly appealing because they are a waste product of ore processing and part of their disposal cost is already included in mine plans. Effluent trace metal levels from tailings columns were generally as low or lower than levels from peat and till columns, although the trace metal removal capacity of tailings was lower than that of peat and till. Tailings also tended to maintain solution pH in an environmentally acceptable range, between 6.8 and 7.8. Tailings were thus selected for field trials, which examined three options for their use in a full-scale treatment system: unsaturated flow beds, saturated flow beds and joint disposal of tailings with waste rock.

The treatment beds reduced trace metal levels in stockpile drainage at tailings:waste rock ratios of 0.0024 to 0.0036 (table 20). Both unsaturated and saturated flow tailings treatment beds reduced copper concentrations below the effluent guideline of 0.15 mg/l for the entire period of study. The number of bed volumes successfully treated for nickel and cobalt ranged from 0 to 50 out of 145 total bed volumes of outflow (table 21). Treatment success for zinc could not be similarly assessed since all of the influent had zinc levels below the 0.75 mg/l guideline concentration, although the beds did remove 33 to 55 pct of the influent zinc.

Joint disposal techniques not only reduced the concentration of trace metals in stockpile effluent but also reduced the overall volume of drainage. Such reductions in the volume of effluent are important in meeting downstream water quality standards. Both the unvegetated and vegetated joint disposal treatments were successful in reducing discharge volume and metal concentrations when compared to the controls (table 22). Both treatments produced effluent that met the copper guideline; the nickel concentration was also reduced, but it nevertheless exceeded the effluent guideline by more than a factor of two. The joint disposal technique also reduces the overall waste storage area. With the joint disposal mixture examined in the present study, a

TABLE 20. - Reductions in Overall Trace Metal Release Produced by Tailings Treatments

Treatment method[1]	Mass of tailings in treatment system, tons	Mass of rock treated, tons	Tailings: rock mass ratio	Reduction in trace metal release[1], pct				
				Cu	Ni	Co	Zn	CEU
Unsaturated flow tailings bed....	2.0	550	0.0024:1	[2]89	24	38	33	42
Saturated flow tailings bed....	1.3	550	0.0036:1	[2]95	9	27	55	37
Joint disposal								
Unvegetated......	7.0	37	0.19:1	[3]78	69	68	80	72
Vegetated........	8.1	37	0.22:1	[3]94	82	87	78	87

[1] All data from 1983 only, except for unsaturated bed, 1982-83.

[2] Mass metal input minus mass output, divided by mass input.

[3] Mass metal output from controls minus mass output from treated bins, divided by mass output from controls.

TABLE 21. - Success of Tailings Treatment Beds in Achieving Effluent Guidelines

Parameter	Guideline limitation	Unsaturated bed, port one[1]		Saturated bed[2]	
		Pct of inflow volume with concentrations exceeding guideline	Pct of outflow volume with concentrations exceeding guideline	Pct of inflow volume with concentrations exceeding guideline	Pct of outflow volume with concentrations exceeding guideline
Cu.....	0.15 mg/l	69	0	88	0
Ni.....	.75 mg/l	100	100	100	91
Co.....	.15 mg/l	97	66	98	81
Zn.....	.75 mg/l	0	0	0	0
pH.....	6.0 to 9.0	0	0	0	0
CEU.....	0.45 mg/l	100	84	100	84

[1] Total outflow volume of 145 bed volumes.

[2] Total outflow volume of 64 bed volumes.

NOTE: High flow periods during which contaminant levels exceeded guideline are excluded.

TABLE 22. - Flow-Weighted Concentrations from Joint Disposal Bins Compared to Effluent Guidelines

Parameter	Guideline limitation	Average flow-weighted concentration		
		Controls	Unvegetated tailings	Vegetated tailings
Cu.......	0.15 mg/l	0.31	0.11	0.06
Ni.......	.75 mg/l	3.2	1.58	1.78
Co.......	.15 mg/l	0.11	0.06	0.05
Zn.......	.75 mg/l	0.23	.07	0.15
TSS.......	20.0 mg/l	[1]1.4	[1]3,200	[1]280
pH.......	6.0 to 9.0	6.0	6.2	6.2
CEU.......	0.45 mg/l	0.75	0.34	0.30

[1] Concentrations given only for period of June to November, 1983, after vegetation of two tailings bins.

minimum of 20 pct of the tailings that would be produced could be deposited within the stockpiles (table 20). Methods that would optimize tailings incorporation into the stockpile would further decrease the tailings storage area.

These test results can be applied to the design of large-scale field tests. Design of large scale treatment beds must consider both the hydraulic and metal removal capacities of the beds. Important considerations in design of a joint disposal system include stabilization of a tailings cap, revegetation, and placement of the tailings in relation to the waste rock. The reduction of suspended solids levels in surface runoff from the system, acceptable designs for liners and underdrains to reduce groundwater seepage, and the susceptibility of the tailings themselves to oxidation and leaching must also be considered in using tailings in treatment systems.

REFERENCES

1. Andersson, L. H., and B. Lindquist. Some Experiments on the Interaction Between Feldspars and Salt Solutions. Geol. Foren. Stockh. Forh., v. 78, 1956, pp. 459-462.

2. Beard, H. R., H. B. Salisbury and M. B. Shirts. Absorption of Radium and Thorium from New Mexico Uranium Mill Tailing Solutions. BuMInes RI 8463, 1980, 14 pp.

3. Bennett, A., and F. Goodridge. Hydrodynamic and Mass Transfer Studies in Packed Absorption Columns. Part I: Axial Liquid Dispersion. Trans. Instn Chem. Engrs, v. 48, 1970, pp. T232-T240.

4. Boelter, D. H. Physical Properties of Peats Related to Degree of Decomposition. Soil. Sci. Soc. Am. Proc., v. 33, 1969, pp. 606-609.

5. Boelter, D. H., and E. S. Verry. Peatland and Water in the Northern Lake States. USDA For. Serv., Gen. Tech. Rep. NC-31, 1977, 22pp.

6. Boorman, R. S., and D. M. Watson. Chemical Processes in Abandoned Sulphide Tailings Dumps and Environmental Implication for Northeastern New Brunswick, CIM Bull., v. 69, no. 773, 1976, pp. 86-96.

7. Borovsky, J. P. Personal communication. Reclamation consultant, Barr Engineering Company, Minneapolis, MN. 1984.

8. Borovsky, J. P., D. F. Grigal and R. L. Strassman. Reclamation of Tailing Basins Resulting from Copper-Nickel Milling. Rept. No. 23/27-155. BuMines, 1983, 147 pp.

9. Broman, P. G. Purification of Industrial and Municipal Waste Water by Means of Mineral Slime. Proc. 11th International Mineral Processing Congress. Univ. Cagliari, Ist. Arte Min. Prep. Miner., Cagliari, Italy, 1975, pp. 1371-1396.

10. Bunzl, K. Kinetics of Ion Exchange in Soil Organic Matter. II. Low Exchange During Continuous Addition of Pb^{2+}-Ions to Humic Acid and Peat. J. Soil Sci., v. 25, 1974, pp. 343-356.

11. _____. Kinetics of Ion Exchange in Soil Organic Matter. III. Differential Ion Exchange Reactions of Pb^{2+}-Ions in Humic Acid and Peat. J. Soil Sci., v. 25, 1974, pp. 517-534.

12. Bunzl, K., W. Schmidt, and B. Sansoni. Kinetics of Ion Exchange in Soil Organic Matter. IV. Adsorption and Desorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ca^{2+} by Peat. J. Soil Sci., v. 27, 1976, pp. 32-41.

13. Busenberg, E. The Products of Interaction of Feldspars with Aqueous Solutions at 25^{o} C. Geochim. Cosmochim. Acta, v. 42, 1978, pp. 1679-1686.

14. Cameron, R. D. Treatment of a Complex Landfill Leachate with Peat. Can. J. Civ. Eng., v. 5, 1978, pp. 83-97.

15. Chamberlain, P. G. Personal communication. Technical project officer, BuMines, Twin Cities, MN, 1984.

16. Chaney, R. L., and P. T. Hundemann. Use of Peat Moss Columns to Remove Cadmium from Wastewaters. J. Water Poll. Control Fed, v. 51, 1979, pp. 17-21.

17. Cole, J. S., and O. R. Matthews. Use of Water by Spring Wheat on the Great Plains. U. S. Dep. Agriculture, Bull. 1004, 1923, 33pp.

18. Coleman, N.T., A. C. McClung, and D. P. Moore. Formation Constants for Cu(II) - Peat Complexes. Sci., v. 123, 1956, pp. 330-331.

19. Coupal, Bernard, and J.-M. Lalancette. The Treatment of Wastewater with Peat Moss. Water Res., v. 10, 1976, pp. 1071-1076.

20. Davis, J. A., and J. O. Leckie. Effect of Adsorbed Ligands on Trace Metal Uptake by Hydrous Oxides. Env. Sci. Technol., v. 12, 1978, pp. 1309-1315.

21. DeMumbrum, L. E., and M. L. Jackson. Infrared Adsorption Evidence on Exchange Reaction Mechanism of Copper and Zinc with Layer Silicate Clays and Peat. Soil Sci. Soc. Am. Proc., v. 20, 1956, pp. 334-337.

22. Diaconescu, E., and F. Chirac. Cation Exchangers from Peat of Dersca-Dorohoi. Bulg. Inst. Politeh. Iasi, v. 15, 1969, Chem. Abstr., v. 74, 1971, no. 1289035.

23. Donovan, R. P., R. M. Felder and H. H. Rogers. Vegetative Stabilization of Mineral Waste Heaps. EPA-60012-76-087, 1976, 305 pp.

24. Dowd, J. E., and D. S. Riggs. A Comparison of Estimates of Michaelis-Menten Kinetic Constants from Various Linear Transformations. J. Biol. Chem. v. 240, No. 2, 1965, pp. 863-869.

25. Dunne, T., and L. B. Leopold. Water in Environmental Planning. W. H. Freeman and Company, San Francisco, CA, 1978, 818 pp.

26. Eger, P., B. Johnson and G. Hohenstein. 1978 DNR/AMAX Field Leaching and Reclamation Program: Progress Report on the Leaching Study. MN Dep. Nat. Resour., 1979, 161 pp.

27. Eger, P., B. Johnson and P. Otterson. Field Studies: Leaching, Metal Transport and Metal Pathways. Preliminary report. Regional Copper-Nickel Study. MN Dep. Nat. Resour., 1977, 151 pp.

28. Eger, P., and K. Lapakko. Leaching and Chemical Transport at the Erie Mining Company Dunka Site: A Data Summary, 1976-1979. MN Dep. Nat. Resour., 1980, 62 pp.

29. _____. The Leaching and Reclamation of Low Grade Mineralized Stockpiles. Paper in Proceedings, 1981 Symposium on Surface Mining Hydrology, Sedimentology, and Reclamation. Univ.of Kentucky, Lexington, KY, 1981, pp. 157-166.

30. Eger, P., K. Lapakko, and P. Otterson. Trace Metal Uptake by Peat: Interaction of a White Cedar Bog and Mining Stockpile Leachate. Paper in 6th International Peat Cong., Duluth, MN, 1980, pp. 542-547.

31. Eger, P., K. Lapakko, and A. Weir. Heavy Metals Study: 1979 Progress Report on the Field Leaching and Reclamation Program and the Removal of Metals from Stockpile Runoff by Peat and Tailings. MN Dep. Nat. Resour., 1980, 95 pp.

32. Ellis, B. G. The Soil as a Chemical Filter. In Recycling Treated Municipal Wastewater and Sludge Through Forest and Cropland, ed. by W. E. Sopper and L. T. Kardos. Univ. of Pennsylvania, University Park, PA, 1973, pp. 46-70.

33. Engineering and Mining Journal. Markets. Engineering and Mining Journal, Vol. 184, no. 10, October 1983, p. 39.

34. Eskenazy, G. Adsorption of Beryllium on Peat and Coals. Fuel, v. 49, 1970, pp. 61-67.

35. _____. Adsorption of Gallium on Peat and Humic Acids. Fuel, v. 46, 1967, pp. 187-191.

36. _____. Adsorption of Titanium on Peat and Coals. Fuel, v. 51, 1972, pp. 221-223.

37. Eswaran, H., and W. C. Bin. A Study of Deep Weathering Profile on Granite in Peninsular Malaysia: III. Alteration of Feldspars. Soil Sci. Soc. Am. J., 1978, pp. 154-158.

38. Exxon Minerals Company. Crandon Project Environmental Impact Report, Ch. 3, Alternatives to the Proposed Action, 1982, 48 pp.

39. Farnham, R. S. Use of Organic Soils for Wastewater Filtration. Ch. in Histosols: Their Characteristics, Use, and Classification. Soil Sci. Soc. Am., 1974, pp. 111-118.

40. Fetter, C. W. Attenuation of Waste Water Elutriated Through Glacial Outwash. Groundwater, v. 15, No. 5, 1977, pp. 365-371.

41. Fraser, D. C. Organic Sequestration of Copper. Econ. Geol., v. 56, 1961, pp. 1063-1078.

42. Freeze, R. A., and J. A. Cherry. Groundwater. Prentice-Hall, 1979, 604 p.

43. Geswein, A. J. Liners for Land Disposal Sites. EPA-SW-137, 975, 66 pp.

44. Golder Associates, Inc. (Atlanta, GA) Underdrain Review, Crandon Project, Waste Disposal System, Project Report 3.2. 1982, 23 pp.

45. Gorham, E. Chemical Studies on the Soil and Vegetation of Water-Logged Habitats in the English Lake District. J. Ecol., v. 41, 1973, pp. 345-360.

46. Griffin, R. A., R. R. Frost, and N. F. Shimp. Effect of pH on Removal of Heavy Metals from Leachates by Clay Minerals. Paper in Residual Management by Land Disposal: Proceedings of Hazardous Waste Research Symposium. EPA-600/9-76-015, 1976, pp. 259-268.

47. Griffin, R. A., and N. F. Shimp. Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals. EPA-600/2-78-157, 1978, 157 pp.

48. Grigal, D. F., and W. S. Nord. Inventory of Heavy Metals in Minnesota Peatlands. University of Minnesota, Department of Soil Science, St. Paul, MN, 1983, 13 pp.

49. Harries, J. R., and A. I. M. Ritchie. The Effect of Rehabilitation on the Oxygen Concentrations in Waste Rock Dumps Containing Pyritic Material. Proc. Symp. Surface Mining Hyd. Sed. Reclam. University of Kentucky, Lexington, KY, 1984, pp. 463-466.

50. _____. Runoff Fraction and Pollution Levels in Runoff from a Waste Rock Dump Undergoing Pyritic Oxidation. Wat. Air Soil Poll., v. 19, 1983, pp. 155-170.

51. Hawkes, H. E., and M. L. Salmon. Trace Elements in Organic Soils as a Guide to Copper Ore. 21st International Geological Congress, Part 2, 1960, pp. 38-43.

52. Hawley, J. R. Mine Waste Control in Ontario. Ontario Ministry of the Environment, Toronto, Ont., Canada, 1977, 241 pp.

53. Healy, T. W. Colloidal Precipitates as Activators and Depressants in Flotation. Proc. Austral. Inst. Min. Met. Conf., W. Austral., 1973, pp. 477-484.

54. Hermsmeier, L. F., L. D. Meyer, A. P. Barnett and R. A. Young. Construction and Operation of a 16-unit Rainulator. ARS 41-62. U. S. Dep. Agriculture, 1963, 136 pp.

55. Herskowitz, M., and J. M. Smith. Trickle-Bed Reactors: A Review. Amer. Inst. Chem. Engr. J., v. 29, 1983, pp. 1-18.

56. Hewett, M. J. Hydrology of Stockpiles of Sulfide Bearing Gabbro in Northeastern Minnesota. MN Dep. Nat. Resour., 1980, 184 pp.

57. Hillel, D. Soil and Water. Academic Press, 1971, 288 pp.

58. Huang, W.H., and W. D. Keller. Dissolution of Rock Forming Silicate Minerals in Organic Acids: Simulated First Stage Weathering of Fresh Mineral Surfaces. Am. Miner, v. 55, 1970, pp. 2076-2094.

59. Huang, W. H., and W. C. Kiang. Laboratory Dissolution of Plagioclase Feldspars in Water and Organic Acids at Room Temperatures. Am. Miner, v. 57, 1972, pp. 1849-1859.

60. Ibarra, J. V., , J. Osacar, and J. M. Gavilan. Retention of Metallic Cations by Lignites and Humic Acids. Fuel, v. 46, 1979, pp. 827-830.

61. Iwasaki, I., A. S. Malicsi and R. J. Lipp. Mineral Processing Studies--Flotation Tests. Final Report to Minnesota Environmental Quality Board, Copper-Nickel Study. MN Environ. Quality Board, 1978, 366 p.

62. Iwasaki, I., A. S. Malicsi, K. A. Smith and B. L. Christensen. A preliminary study of release and removal of copper and nickel ions in mine and mill effluents. Proc. 49th Ann. Meeting, Minn. Section AIME and 37th Ann. Min. Sym., Jan. 1976, pp. 26.1-26.31.

63. Iwasaki, I., K. A. Smith and A. S. Malicsi. By-product Recovery from Copper-Nickel Bearing Duluth Gabbro. University of Minnesota, Mineral Resources Research Center, Minneapolis, MN, 1982, 283 p.

64. James, R. O., and T. W. Healy. Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface. 1. Co (II) Adsorption on SiO_2 and TiO_2 as Model Systems. J. Colloid Interface Sci., v. 40, 1972, pp. 42-52.

65. _____. Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface. 2. Charge Reversal of SiO2 and TiO2 Colloids by Adsorbed Co(II), La (III), and Th (IV) as Model Systems. J. Colloid Interface Sci., v. 40, 1972, pp. 53-64.

66. Jaynes, D. B., A. S. Rogowski and E. L. Jacoby, Jr. Spoil atmosphere in reclaimed coal strip-mines. Pennsylvania State Univ., University Park, PA, 1982, 20 pp.

67. Johnson, M. D., and G. A. Lieberman. Aquatic Biology Resources. In Regional Copper-Nickel Study, v. 4, ch. 1. Minnesota State Planning Agency, St. Paul, MN, 1979, 110 p.

68. Keller, W. D., and A. L. Reesman. Dissolved Products of Artificially Pulverized Silicate Minerals and Rocks: Part 2. J. Sed. Petrology, v. 33, pp. 426-437.

69. Kernik, L. D. Elemental Composition of Hare Browse in Relation to Site Factors in Northeastern Minnesota. M.S. Thesis. Univ. MN, St. Paul, MN, 1981, 155 pp.

70. Kingston, G. A., F. V. Carillo, J. J. Gray, and P. McIlroy. Availability of U.S. Primary Nickel Resources. U.S. BuMines IC 8469, 1970, 57pp.

71. Klute, A., and D. F. Heermann. Water Movement in Uranium Mill Tailings Profiles. EPA Technical Note ORP/LV-78-8. 1978, 81 pp.

72. Kosowski, Z. V. Control of Mine Drainage from Coal Mine Mineral Wastes. Phase II. Pollution Abatement and Monitoring. EPA-R2-73-230. 1973, 83 pp.

73. Kotkovskii, A. P., L. V. Kosongova, and N. S. Volosovich. Polyfunctional Cation Exchangers from Peat and Peat Semicoke. Vessi. Akad. Nauk Belarus., SSR, Ser. Khim. Nauk, v. 86, No. 3, 1973, pp. 86-89; Chem Abstr., v. 80, 1974, no. 72652p.

74. Kotkovskii, L. V. Kosongova, N. S. Volosovich, and S. V. Kashirina. Production of Sulfonated Cation Exchangers from Coke and Peat Semicoke. Pererab. Ispol'z. Torfa Sapropelei, 1971, pp. 163-167; Chem Abstr., v. 78, 1973, no. 60579r.

75. Kurdi, F., and H. E. Doner. Zinc and Copper Sorption and Interaction in Soils. Soil Sci. Soc. Am. J., v. 47, 1983, pp. 873-876.

76. Lai, S.-H., and J. J. Jurinak. The Transport of Cations in Soil Columns at Different Pore Velocities. Soil Sci. Soc. Amer. Proc., v. 36, 1972, pp. 730-733.

77. Lapakko, K. Estimation of Particle Size Distribution: Run-of-mine Waste Rock and Primary Crusher Products. MN Environ. Quality Board, 1978, 3 pp.

78. Lapakko, K. A. Kinetics and Mechanisms of the Oxidative Dissolution of Metal Sulfide and Silicate Minerals Present in the Duluth Gabbro. M.S. Thesis. Univ. MN, Minneapolis, MN, 1980, 199 pp.

79. Lapakko, K. A., Eger, A. P., and J. D. Strudell. Trace Metal Removal from Copper-Nickel Mine Stockpile Drainage, MN Dep. Nat. Resour., 1985, 202 pp.

80. Lapakko, K. A., Strudell, J.D., and A. P. Eger. Low-Cost Removal of Trace Metals from Copper-Nickel Mine Stockpile Drainage. Volume II, Trace Metal Sequestration by Peat, Other Organics, Tailings and Soils: A Literature Review (contract J0205047). BuMines OFR, 1986, 45 pp.

81. Lind, D., T. Halpern and M. D. Johnson. The Toxicity of Heavy Metals, Beneficiation Reagents and Hydrogen Ion to Aquatic Organisms. Regional Copper-Nickel Study. MN Environ. Quality Board, 1978, 181 pp.

82. Listerud, W. H., and D. G. Meineke. Mineral Resources of a Portion of the Duluth Complex Adjacent Rocks in St. Louis and Lake Counties in Northeastern Minnesota. MN Dep. Nat. Resour. Rep. 93, 49 pp.

83. Lovering, T. S. Organic Precipitation of Metallic Copper. U.S. Geol. Survey Bull. 795-C, 1927, pp. 45-52.

84. Manskaya, S. M., T. B. Drosdova, and M.P. Emel'yanova. Distribution of Copper in Peats and Peat Soils of the Belorussian SSR. Geokhimiya, v. 6, 1960, pp. 630-643.

85. Meineke, D. G., M. K. Vadis, and A. W. Klaysmat. Pilot Study on Peat Exploration Geochemistry, Birch Lake Area, Lake County, Minnesota. MN Dep. Nat. Resour. Report 108-1, 1977, 10 pp.

86. Miller, J. D. Removal of Dissolved Contaminants from Mine Drainage. Office of Research and Monitoring. EPA-R2-72-130, 1972, 62 pp.

87. Minnesota Environmental Quality Board. Regional Copper-Nickel Study, Executive Summary. MN State Planning Agency, St. Paul, MN, v. 1, 1980, 118 pp.

88. Mumpton, F. A., and R. A. Sheppard. Zeolites. Geotimes, v. 17, 1972, pp. 16-17.

89. Naismith, N. W., and W. G. Kirchner. Liquid Dispersion in Trickle Flow through Ore Dumps. In Trudinger, P.A., M. R. Walter and B. J. Ralph, eds. Biogeochemistry of Ancient and Modern Environments. Springer, 1980, pp. 545-555.

90. Nelson, J. D., and T. A. Shepherd. Overview, Seepage Control. Report for Royal Commission of Inquiry, Health and Environmental Protection, Uranium Mining, Province of British Columbia, 1979, 71 pp.

91. Nelson, M. The Oxidation Dissolution of Ferrous Monosulfides and Behavior of Associated Trace Metals. Ph. D. Thesis, Stanford Univ., Palo Alto, CA, 1978, 299 pp.

92. Nixon, R. A. Differences in Incongruent Weathering of Plagioclase and Microcline: Cation Leaching Versus Precipitates. Geol., v. 7, 1979, pp. 221-224.

93. Olcott, P. G., and D. I. Siegel. Physiography and Surficial Geology of the Copper-Nickel Study Region, Northeastern Minnesota. U. S. Geol. Surv. WRI 78-51, 1978, 22 pp.

94. Olson, J. J. The Effects of Heavy Metals on the Germination and Radicle Growth of Some Forest Plants of Northern Minnesota. Regional Copper-Nickel Study. MN Environ. Quality Board, 1978, 35 pp.

95. Oreshko, V. F., A. I. Berdnikov, and V. V. Przhbyl'skii. The Sorption of Radioactive Cobalt on Peat. Radiokhimiya 4, 1962, pp. 499-502.

96. Owen Ayres and Associates, Inc. (Eau Claire, WI) Waste Disposal Facility, Reclamation Cap, Crandon Project, Water Balance Analysis. Unpublished report prepared for Exxon Minerals Company-Crandon Project. 1982, pp. 45-50.

97. Parkash, S., and R. A. Brown. Use of Peat and Coal for Recovering Zirconium from Solution. CIM Bull., v. 69, 1976, pp. 69-64.

98. Pickering, W. F. Copper Retention by Soil/Sediment Components. In Copper in the Environment, ed. by J. O. Nriagu. Wiley, 1979, pp. 217-253.

99. Pierce, F. J. The Content and Distribution of Cd, Cr, Cu, Ni, Pb, and Zn in 16 Selected Minnesota Soil Series. M. S. Thesis. Univ. MN, St. Paul, MN, 1980, 137 pp.

100. Plonke, H. B., and A. S. Rogowski. How Effective Is the Deep Placement of Acid Spoil Materials? Paper in Canadian Land Reclamation Assoc. 4th Conf. Saskatchewan, 1979, pp. 87-104.

101. Prchlik, J., J. Soukup, K. Kolomaznik, V. Zapletal and V. Ruzicka. Liquid Distribution in Columns and Reactors Filled with Irrigated Dumped Packing. Intl. Chem. Engr., v. 15, 1975, pp. 125-135.

102. Premi, P. R. Effect of Different Levels of Copper and Zinc Added as Adsorbed Cations on Purified Peat and Sewage on Nitrogen Mineralization During Incubation of Soil. Agrochem., v. 14, 1970, 372 pp.

103. Prettyman, D. H. Soil Survey of Kawishiwi Area, Minnesota. U. S. Dep. Agriculture, 1978, 35 pp.

104. Randall, J. M. Variations in Effectiveness of Barks as Scavengers for Heavy Metal Ions. Forest Prod. J., v. 27, 1977, pp. 51-56.

105. Rutherford, G. K., D. Dimma, G. W. Van Loon and W. G. Breck. The Pedological Properties of Tailings Derived from Three Mining Operations in the Sudbury Area, Ontario, Canada. J. Environ. Qual., v. 11, no. 3, 1982, pp. 511-518.

106. Ryss, K. A., and M. R. Hoffmann. Removal of Trace Metals from Aqueous Systems by Adsorption on Peat Bog Material. Report to MN Environ. Quality Council, 1979, 21 pp.

107. Scales, M. Pyrrhotite Removal Cuts Inco Sulphur Dioxide Levels. Can. Min. J., v. 105, no. 3, 1984, pp. 39-44.

108. Schalscha, E. B., H. Appelt, and A. Schatz. Chelation as a Weathering Mechanism: I. Effect of Complexing Acids on the Solubilization of Iron from Minerals and Granodiorite. Geochim. Cosmochim. Acta, v. 31, 1967, pp. 587-596.

109. Schluter, R. B., and W. M. Mahan. Flotation Responses of Two Duluth Complex Copper-Nickel Ores. BuMines RI 8509. 1981, 24 pp.

110. Schnitzer, M., and S. U. Khan. Humic Substances in the Environment. Dekker, 1972, 327 pp.

111. Semmens, M. J., and W. Martin. Studies on Heavy Metal Removal from Saline Waters by Clinoptilolite. Paper in AIChE Symp. Series, 1980, pp. 367-376.

112. Semmens, M. J., and M. Seyfarth. The Selectivity of Clinoptilolite for Certain Heavy Metals. Paper in Natural Zeolites: Occurrence, Properties, Use, ed. by L. B. Sand and Mumpton, Pergamon, 1978, pp. 517-526.

113. Siegel, D. I. Hydrogeochemistry and Kinetics of Silicate Weathering in a Gabbroic Watershed: Filson Creek, Northeastern Minnesota. Ph.D. Thesis. Univ. MN, Minneapolis, MN, 1981, 275 pp.

114. Siegel, D. I., and D. W. Ericson. Hydrology and Water Quality of the Copper-Nickel Study Region, Northeastern Minnesota. U. S. Geol. Surv. WRI 80-739. 1980, 87 pp.

115. Smith, E. F., P. MacCarthy, T. C. Yu, and H. B. Mark. Sulfuric Acid Treatment of Peat for Cation Exchange. J. Water Poll. Control Fed., v. 49, 1977, pp. 633-638.

116. Soderberg, R. L., and R. A. Busch. Design Guide for Metal and Nonmetal Tailings Disposal. BuMines IC 8755. 1977, 136 pp.

117. Stevenson, R. J., P. J. Kreisman and N. P. Sather. Minnesota Regional Copper-Nickel Study. Vol. 3, Ch. 1, Geology and Mineralogy. MN Environ. Quality Board, 1979, 70 pp.

118. Stumm, W., and J. J. Morgan. Aquatic Chemistry. Interscience, 1981, 780 pp.

119. Sturgess, J. Personal communication, 1981; available from J. Sturgess, Cypress Mines, Inc., Challis, ID.

120. Sung, W., and J. J. Morgan. Kinetics and Products of Ferrous Iron Oxygenation in Aqueous Systems. Environ. Sci. Technol., v. 14, 1980, pp. 461-468.

121. Szabo, I. Adsorption of Cations on Humus Preparations. Comm. Third Math-Phys. Class Hung. Acad. Sci., v. 8, 1958, pp. 393-402.

122. Theis, T. L., and R. O. Richter. Chemical Speciation of Heavy Metals in Power Plant Ash Pond Leachate. Environ. Sci. Technol., v. 13, 1979, pp. 219-224.

123. Thingvold, D., P. Eger, M. Hewett, B. Honetschlager, K. Lapakko and R. Mustalish. Minnesota Regional Copper-Nickel Study. v. 3, Ch. 4, Water Resources. MN Environ. Quality Board, 1979, 206 pp.

124. Trethewey, W. D. The Utilization of Copper-Nickel Tailing. Univ. MN, Miner. Resour. Res. Center, Minneapolis, MN, 1977, 15 pp.

125. U. S. Bureau of Land Management. Weight Estimate Forage Survey Handbook. 1963, 41 pp.

126. U. S. Environmental Protection Agency. Development Document for Effluent Limitations Guidelines and Standards for the Ore Mining and Dressing Point Source Category. EPA 44011-82/061. 1982, 656 pp.

127. Van Genuchten, M. Th., J. M. Davidson and P. J. Wierenga. An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement through Porous Media. Soil Sci. Soc. Am. Proc., v. 38, 1974, pp. 29-35.

128. Veith, D. L., P. J. Kreisman and R. H. Poppe. Minnesota Regional Copper-Nickel Study. Vol. 2, Ch. 2, Mineral Extraction. MN Environ. Quality Board, 1979, 79 pp.

129. _____ . Minnesota Regional Copper-Nickel Study. v. 2, Ch. 3, Mineral Processing. MN Environ. Quality Board, 1979, 102 pp.

130. _____. Minnesota Regional Copper-Nickel Study. v. 2, Ch. 5, Integrated Development Models. MN Environ. Quality Board, 1979, 55 pp.

131. Vuceta, J., and J. J. Morgan. Chemical Modelling of Trace Metals in Fresh Waters: Role of Complexation and Adsorption. Environ. Sci. Technol., v. 12, 1978, pp. 1302-1309.

132. Walmsley, M. E. Physical and Chemical Properties of Peat. Ch. in N.W. Radforth and C. O. Brawner, eds., Muskeg and the Northern Environment in Canada. University of Toronto Press, Toronto, Ont., Can., 1973, pp. 82-129.

133. Wentink, G. R., and J. E. Etzel. Removal of Metal Ions by Soil. J. Water Poll. Control Fed., v. 44, 1972, pp. 1561-1574.

134. Wilson, M. J. A Study of Weathering in a Soil Derived from a Biotite Hornblende Rock. 1. Weathering of Biotite. Clay Miner., v. 8, 1970, pp. 291-303.

135. Wojciechowski, B. W. Chemical Kinetics for Chemical Engineers. Sterling Swift Publ. Co., 1975, 333 pp.

136. Young, R. Personal communication. U. S. Department of Agriculture, North Central Research Laboratory, Morris, MN, 1983.