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Removal of Metal Cations from Water Using Zeolites

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Abstract

Zeolites from abundant natural deposits were investigated by the Bureau of Mines for efficiently cleaning up mining industry wastewaters. Twenty-four zeolite samples were analyzed by x-ray diffraction and inductively coupled plasma. These included clinoptilolite, mordenite, chabazite, erionite, and phillipsite. Bulk densities of a sized fraction (−40, +65 mesh) varied from 0.48 to 0.93 g/mL. Attrition losses ranged from 1 to 18% during an hour-long shake test. The 24 zeolites and an ion-exchange resin were tested for the uptake of Cd, Cu, and Zn. Of the natural zeolites, phillipsite proved to be the most efficient, while the mordenites had the lowest uptakes. Sodium was the most effective exchangeable ion for exchange of heavy metals. Wastewater from an abandoned copper mine in Nevada was used to test the effectiveness of clinoptilolite for treating a multi-ion wastewater. The metal ions Fe^{3+}, Cu^{2+}, and Zn^{2+} in the copper mine wastewater were removed to below drinking water standards, but Mn^{2+} and Ni^{2+} were not. Calcium and NH_4^+ interfered with the uptake of heavy metals. Adsorbed heavy metals were eluted from zeolites with a 3% NaCl solution. Heavy metals were concentrated in the eluates up to 30-fold relative to the waste solution. Anions were not adsorbed by the zeolites.

INTRODUCTION

Federal and state pollution-control standards for heavy metal content of water from mineral processing operations have become more stringent in recent years. Metal removal is often accomplished by precipitating hydrous oxides by CaO addition. Although this method is relatively simple and inexpensive, it does have the following disadvantages: 1) it generates a large volume of sludge which is costly to dispose of and, in some cases, can be classified as hazardous; 2) at around 4°C the precipitation layer in settling ponds undergoes an inversion which results in mixing of the solids and liquids; 3) it may not produce an effluent sufficiently low in heavy metal content; and 4) the metal values are lost (*1*).

To help meet present and possibly more stringent future Environmental Protection Agency (EPA) and state requirements, the U.S. Bureau of Mines is investigating new or alternative methods for removing heavy metals from wastewater. As part of the program, naturally occurring zeolites are being explored as ion exchangers to exchange the heavy metal ions with sodium ions.

There are more than 30 distinct species of zeolite that occur in nature. However, only seven, mordenite, clinoptilolite, ferrierite, chabazite, erionite, phillipsite, and analcime, occur in sufficient quantity to be considered as viable mineral resources (*3*).

Zeolites are aluminosilicate minerals that contain alkali and alkaline-earth metals, such as sodium, calcium, and potassium, as well as water, in their structural framework. The physical structure is porous, enclosing interconnected cavities in which the metal cations and water molecules are contained. The zeolites have reversible hydration properties in addition to their cation-exchange properties (*2*).

The fundamental building block of the zeolites is a tetrahedron of four oxygen atoms surrounding a relatively small silicon or aluminum atom. The structure consists of SiO_4 and AlO_4 tetrahedra arranged so that each oxygen atom is shared between two tetrahedra. Because aluminum has one less positive charge than silicon, the framework has a net negative charge of one at the site of each aluminum atom and is balanced by the exchangeable cation (*4*). Maximum substitution of Al^{3+} for Si^{4+} results in an Si/Al ratio of 1. Thomosonite, gismondine, and gonnardite are the only natural zeolites that have Si/Al ratios close to 1 (*5*).

The objective of this investigation was to determine the efficiency of zeolites in removing a variety of cations from actual and synthetic solutions and waste streams. Since the goal was to reduce impurities to below drinking water standards, Table 1 containing the EPA standards is included for reference (*6*).

TABLE 1
EPA Drinking Water Standards

Metal ion	Drinking water concentration (mg/L)
Cd	0.01
Cr	0.05
Cu	1
Fe	0.3
Mn	0.05
Ni	0.015
Pb	0.05
Zn	5

TEST MATERIALS AND SOLUTIONS

Zeolites

Tests were conducted on 24 natural zeolites from several states in the western United States. Phillipsite, erionite, chabazite, mordenite, and clinoptilolite were represented. In addition, tests were made using a commercial cat litter (mostly mordenite) and using Dowex 50X-18 ion-exchange resin for comparison. The zeolites were used as received, except that some had to be ground to the proper size of −20, +60 mesh for the shake tests. Tests on clinoptilolite were conducted because it is the most abundant and widely available.

Simulated Wastewater Solutions

In wastewaters, the metal ions are predominately present in the sulfate form. Metal sulfates were generally difficult to dissolve, and as a result, the experimental solutions were made from chlorides except for lead, which was made from lead nitrate, and copper, which was used in the sulfate form. These solutions were at a natural pH of 5 to 7. A 3% sodium chloride solution was used to elute the metal ions from the loaded zeolites. Simulated Berkeley Pit water was made using the aforementioned forms, and the pH was adjusted to that of actual Berkeley Pit water, which is about 1.85. The Berkeley Pit is a large Superfind site in Montana that was previously an open pit copper mine. The mine is filling with acidic water (pH 2.5) containing dissolved metals. The water contained, in mg/L, 180 Al, 530 Ca, 2.9 Cd, 180 Cu, 750 Fe, 230 Mg, 140 Mn, 24 K, 79 Na, 380 Zn.

Mine Waste Stream

Wastewater was obtained from an abandoned copper mine tailings pond at the Rio Tinto mine in northeastern Nevada. This wastewater had a pH of 2.62 and contained, in mg/L, 73 Al, 550 Ca, 27 Cu, 210 Fe, 22 Mn, 1.4 Pb, and 11 Zn. This wastewater was used because it is representative of acid mine waters.

EXPERIMENTAL PROCEDURE AND RESULTS

Composition and Mechanical Properties

Table 2 contains the results of x-ray diffraction and inductively coupled plasma spectroscopy analyses for 24 natural zeolites. The clinoptilolites are well represented because they are the most common zeolites. A lower Si/Al ratio means a higher zeolite loading capacity (*6*).

Bulk density, loading capacity, and attrition must be considered when selecting a zeolite based on performance at the lowest possible cost. As

TABLE 2
Zeolite X-Ray Diffraction and ICP Analyses

Type of zeolite	Location	X-Ray	Si/Al ratio
Chabazite	Bowie, AZ	Major: Chabazite Trace: Erionite	3.8
	Christmas, AZ	Major: Chabazite Minor: Quartz	3.2
Clinoptilolite	Barstow, CA	Major: Clinoptilolite Minor: Quartz	5.1
	Buckhorn, NM	Major: Clinoptilolite	4.6
	Castle Creek, ID	Major: Clinoptilolite	4.5
	Creede, CO	Major: Clinoptilolite, feldspar Minor: Cristobalite Trace: Quartz, mica	5.0
	Death Valley Junction, CA	Major: Clinoptilolite	5.4
	Ash Meadows, NV	Major: Clinoptilolite Minor: Quartz	5.7
	Fish Creek Mountains, NV	Major: Clinoptilolite Major: Quartz	4.8
	Hector, CA	Major: Clinoptilolite Intermediate: Quartz Minor: Mordenite	5.4
	Mountain Green, UT	Major: Clinoptilolite	5.6
	Sheaville, OR	Major: Clinoptilolite	5.3
	Mudhill, CA	Major: Clinoptilolite Minor: Quartz, calcite, feldspar	5.4
	Sweetwater, WY	Major: Clinoptilolite	4.5
	Owyhee County, ID	Major: Clinoptilolite Intermediate: Gmelinite	5.2
	Oreana, ID	Major: Clinoptilolite Minor: Cristobalite Trace: Feldspar	5.4
	Houston, TX	Major: Clinoptilolite Minor to major: Amorphous Trace: Quartz, feldspar	
Erionite	Pine Valley, NV	Major: Erionite	3.7
	Shoshone, CA	Major: Erionite Minor: Phillipsite Trace: Clinoptilolite, quartz	4.3
Mordenite	Middlegate, NV	Major: Mordenite Minor: Clinoptilolite, fluorite Trace: Calcite, quartz	5.7
	Cat litter	Major: Mordenite Intermediate: Clay Minor: Fluorite, quartz	5.7
	Lovelock, NV	Major: Mordenite Minor: Cristobalite, feldspar Trace: Quartz, mica	6.0
	Union Pass, AZ	Major: Mordenite	5.5
Phillipsite	Pine Valley, NV	Major: Phillipsite Trace: Quartz	3.6

TABLE 3
Zeolite Bulk Density (−42, +65 mesh)

Type of zeolite	Location	Bulk density (g/mL)
Chabazite	Bowie, AZ	0.59
	Christmas, AZ	0.63
Clinoptilolite	Death Valley Junction, CA	0.93
	Ash Meadows, NV	0.91
	Mud Hill, CA	0.88
	Mountain Green, UT	0.88
	Creede, CO	0.82
	Fish Creek Mountains, NV	0.87
	Barstow, CA	0.78
	Hector, CA	0.75
	Sweetwater, WY	0.75
	Sheaville, OR	0.66
	Buckhorn, NM	0.64
	Owyhee County, ID	0.53
	Castle Creek, ID	0.48
	Oreana, ID	0.75
	Houston, TX	0.88
Erionite	Pine Valley, NV	0.60
	Shoshone, CA	0.63
Mordenite	Middlegate, NV	0.46
	Cat litter	0.48
	Lovelock, NV	0.64
	Union Pass, AZ	0.90
Phillipsite	Pine Valley, NV	0.67

zeolite capacity is measured per unit of weight, bulk density is important for process design. Table 3 shows the measured bulk density of several zeolite samples ground to −40, +65 mesh. Clinoptilolite and mordenite, for which there were several samples, showed a wide range of bulk densities. Attrition tests were made by placing 25 g dry zeolite (−20, +60 mesh) in a 250-mL volumetric flask with 75 mL deionized water. The flask was shaken at 150 rpm for 1 h by a Fisher Versa-Bath.* The zeolite was then thoroughly dried and screened through a 100-mesh screen. The weight of the −100 mesh fraction was used to calculate the percent attrition. Table 4 shows the percent loss due to attrition of 12 zeolites tested.

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*Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

TABLE 4
Attrition Loss

Type of zeolite	Percent loss
Clinoptilolite, Ash Meadows, NV	1.0
Phillipsite, Pine Valley, NV	3.8
Mordenite, Lovelock, NV	3.5
Clinoptilolite, Buckhorn, NM	9.2
Mordenite, Union Pass, AZ	1.0
Clinoptilolite, Creede, CO	8.0
Chabazite, Bowie, AZ	16.6
Chabazite, Christmas, AZ	17.7
Clinoptilolite, Sheaville, OR	11.8
Erionite, Pine Valley, NV	3.8
Clinoptilolite, Hector, CA	2.1
Erionite, Shoshone, CA	9.2

Shake Test

To determine the effect of the Si/Al ratio on uptake in shake tests, 1 g of zeolite (−10, +50 mesh) was placed in each of three 250 mL Erlenmeyer flasks. Then, either 25, 50, or 100 mL of 0.04 *N* lead acetate solution (pH 5) was added to each flask. The flasks were vigorously shaken for 20 h. Cation uptakes were calculated from solution analyses. These results are shown in Table 5. Order of efficiency as shown by these lead adsorption experiments is as follows:

phillipsite > chabazite > erionite > clinoptilolite > mordenite

This correlates with the corresponding Si/Al ratios as shown in Fig. 1.

Column Tests

Loading

All column tests were conducted using 30-cm by 1.0-cm-diameter glass columns topped by a 500-mL head of solution. To determine single metal ion loading capacities for 24 zeolites and the ion-exchange resin, 500 mL of single metal solution (500 ppm) was passed through each column at a flow rate of 1 mL/min (1.3 cm/min linear flow rate). Without changing the zeolite beds, more 500 mL solution batches were passed through the column. The single metal concentrations were measured for the head and tail of each 500 mL portion. The test was concluded when the effluent concentration equalled the head concentration. The capacity is the sum of the uptakes. Column tests were chosen instead of shake tests because columns are more likely to be used in actual applications.

TABLE 5
Capacity of Zeolites for Lead

Material tested	Volume of 0.04 *N* solution (mL)	Meq cation/g zeolite
Chabazite:		
Bowie, AZ	25	0.91
	50	1.35
	100	1.64
Clinoptilolite:		
Ash Meadows, NV	25	0.68
	50	0.87
	100	1.06
Barstow, CA	25	0.80
	50	1.06
	100	1.25
Buckhorn, NM	25	0.51
	50	0.78
	100	0.97
Castle Creek, ID	25	0.54
	50	0.89
	100	1.06
Creede, CO	25	0.43
	50	0.48
	100	0.58
Death Valley, CA	25	0.52
	50	0.82
	100	1.06
Fish Creek Mtns., NV	25	0.38
	50	0.48
	100	0.58
Hector, CA	25	0.95
	50	1.30
	100	1.54
Mtn. Green, UT	25	0.70
	50	0.92
	100	1.06
Sheaville, OR	25	0.50
	50	0.73
	100	0.97
Mudhill, CA	25	0.77
	50	1.01
	100	1.16
Sweetwater, WY	25	0.82
	50	1.11
	100	1.25
Oreana, ID	25	0.51
	50	0.63
	100	0.77
Owyhee County, ID	25	0.43
	50	0.48
	100	0.58

(*continued*)

TABLE 5 (*continued*)

Material tested	Volume of 0.04 *N* solution (mL)	Meq cation/g zeolite
Erionite:		
Pine Valley, NV	25	0.54
	50	1.04
	100	1.54
Shoshone, CA	25	0.54
	50	1.06
	100	1.25
Mordenite:		
Middlegate, NV	25	0.36
	50	0.53
	100	0.58
Lovelock, NV	25	0.27
	50	0.34
	100	0.39
Phillipsite:		
Pine Valley, NV	25	0.55
	50	1.06
	100	1.79

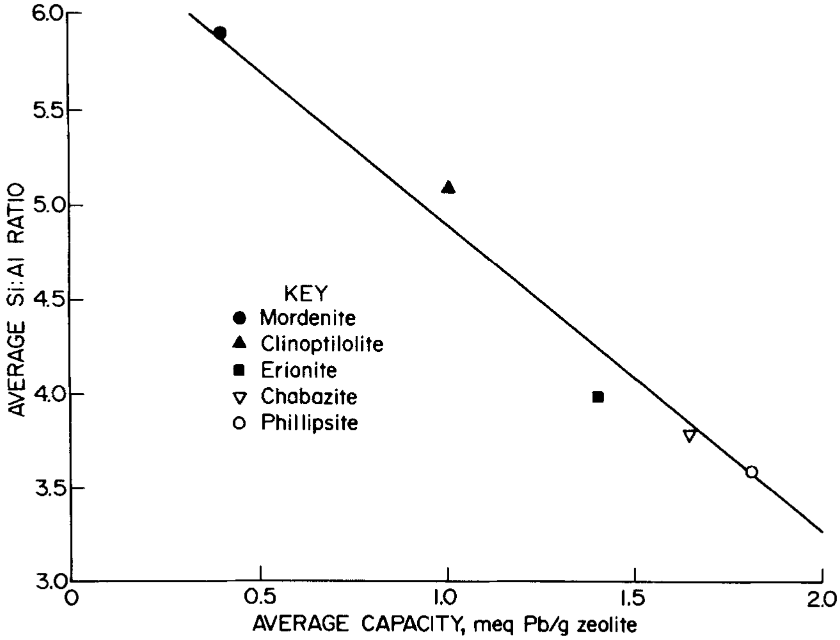

FIG. 1. Correlation between lead capacity and Si/Al ratio.

Table 6 contains the results for cadmium in milliequivalents/gram. Of the natural zeolites, phillipsite had the highest capacity of 2.30. Erionite, on average, had a capacity of 1.59, chabazite 1.57, clinoptilolite 0.95, and mordenite 0.57. The phillipsite had almost as high a capacity as the ion-exchange resin (2.62). Table 7 contains the results for copper. Of the natural zeolites, phillipsite had the highest capcity of 2.73. Erionite, on average, had a capacity of 2.13, chabazite 1.91, clinoptilolite 1.01, and mordenite 0.75. Here again the phillipsite had almost as high a capacity as the resin (2.77). Table 8 contains the results for zinc. Erionite, on average, had a capacity of 1.48, chabazite 1.31, clinoptilolite 0.73, and mordenite 0.42. Overall, the zeolites have the highest capacity for copper, followed by cadmium and finally zinc. This holds true among all the zeolite types.

TABLE 6
Capacity of Zeolites for Cadmium

Type of zeolite	Capacity (meq/g)
Dowex 50W-X8 resin	2.61
Phillipsite, Pine Valley, NV	2.30
Erionite, Pine Valley, NV	1.90
Chabazite, Bowie, AZ	1.74
Clinoptilolite, Hector, CA	1.69
Chabazite, Christmas, AZ	1.39
Clinoptilolite, Barstow, CA	1.37
Erionite, Shoshone, CA	1.28
Clinoptilolite, Sweetwater, WY	1.26
Clinoptilolite, Buckhorn, NM	1.20
Clinoptilolite, Owyhee Co., ID	1.20
Clinoptilolite, Castle Creek, ID	1.14
Clinoptilolite, Sheaville, OR	1.09
Clinoptilolite, Death Valley Junc., CA	1.03
Clinoptilolite, Ash Meadows, NV	0.91
Clinoptilolite, Mudhill, CA	0.75
Clinoptilolite, Creede, CO	0.68
Clinoptilolite, Mtn. Green, UT	0.66
Mordenite, Middlegate, NV	0.66
Clinoptilolite, Oreana, ID	0.56
Mordenite, Union Pass, AZ	0.55
Cat litter	0.55
Mordenite, Lovelock, NV	0.51
Clinoptilolite, Fish Creek Mtns., NV	0.50
Clinoptilolite, Houston, TX	0.40

TABLE 7
Capacity of Zeolites for Copper

Zeolite type and location	Capacity (meq/g)
Dowex 50W-X8 resin	2.77
Phillipsite, Pine Valley, NV	2.73
Erionite, Pine Valley, NV	2.15
Chabazite, Bowie, AZ	2.12
Erionite, Shoshone, CA	2.11
Clinoptilolite, Hector, CA	1.88
Chabazite, Christmas, AZ	1.69
Clinoptilolite, Castle Creek, ID	1.48
Clinoptilolite, Sweetwater, WY	1.47
Clinoptilolite, Barstow, CA	1.31
Clinoptilolite, Ash Meadows, NV	1.18
Clinoptilolite, Death Valley Junction, CA	1.13
Mordenite, Middlegate, NV	1.05
Clinoptilolite, Mudhill, CA	0.98
Cat litter	0.96
Clinoptilolite, Mountain Green, UT	0.86
Clinoptilolite, Buckhorn, NM	0.82
Clinoptilolite, Owyhee Co., ID	0.82
Clinoptilolite, Sheaville, OR	0.76
Clinoptilolite, Fish Creek Mtns., NV	0.63
Clinoptilolite, Oreana, ID	0.63
Mordenite, Lovelock, NV	0.63
Clinoptilolite, Creede, CO	0.55
Mordenite, Union Pass, AZ	0.35
Clinoptilolite, Houston, TX	0.33

Elution

A series of tests was performed to determine if the concentration of metal ions could be increased in the eluate relative to the head solution. Three liters of water containing 10 mg/L of the subject metal ion were put through each column containing Owyhee County, ID, clinoptilolite. Then, 100 mL of 3% NaCl solution was passed through each column at 1 mL/min. The elution was considered successful if all of the loaded metals were completely eluted. The Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} were totally eluted from the zeolites, whereas only 50% of the lead was eluted.

Competing Ions

To test the effect of competing cations on zeolite capacity, a solution containing 10 mg/L of the metal ion of interest and 50 mg/L of the competing ion was passed through a column of Owyhee County, ID, clinop-

TABLE 8
Capacity of Zeolites for Zinc

Zeolite type and location	Capacity (meq/g)
Dowex 50W-X8 resin	2.61
Erionite, Pine Valley, NV	1.68
Chabazite, Bowie, AZ	1.35
Clinoptilolite, Hector, CA	1.35
Erionite, Shoshone, CA	1.28
Chabazite, Christmas, AZ	1.23
Phillipsite, Pine Valley, NV	1.20[a]
Clinoptilolite, Sweetwater, WY	1.08
Clinoptilolite, Castle Creek, ID	0.99
Clinoptilolite, Death Valley Junction, CA	0.86
Clinoptilolite, Mudhill, CA	0.86
Clinoptilolite, Owyhee Co., ID	0.82
Clinoptilolite, Barstow, CA	0.79
Clinoptilolite, Buckhorn, NM	0.79
Clinoptilolite, Ash Meadows, NV	0.76
Mordenite, Middlegate, NV	0.72
Clinoptilolite, Sheaville, OR	0.65
Cat litter	0.67
Clinoptilolite, Mountain Green, UT	0.61
Clinoptilolite, Creede, CO	0.44
Clinoptilolite, Oreana, ID	0.43
Clinoptilolite, Fish Creek Mtns., NV	0.35
Mordenite, Lovelock, NV	0.18
Clinoptilolite, Houston, TX	0.17
Mordenite, Union Pass, AZ	0.12

[a] Test still in progress.

tilolite. The concentration of the competing ion was then raised and the test repeated. This sequence continued until the effluent analysis revealed that the metal ion of interest was not being completely removed. Table 9 shows the concentration of each competing ion which began to affect the uptake of the metal ion of interest. Nickel uptake was affected by low concentrations of calcium, sodium, and ammonia, while concentrations of 1500 mg/L Na^+ and Ca^{2+} had no effect on the uptake of lead.

Exchangeable Ions

Exchangeable ion tests were performed by first passing 500 mL of the exchangeable ion (3%) through the column to displace the existing exchangeable ions. Then, a solution containing 3000 mg/L lead (pH 5) was passed through the column. The results of the exchangeable ion tests are

TABLE 9
Results of Competing Ion Tests

	Competing ions (mg/L)		
	Na^+	Ca^{2+}	NH_4^+
Cd	450	93	300
Co	570	89	220
Cu	940	310	320
Ni	210	44	130
Pb	>1,500	>1,500	300
Zn	710	62	220

shown in Table 10. The best exchangeable ions for lead uptake are ammonium and sodium, while the worst is magnesium. The order of exchangeable ions for lead sorption is Na^+, $NH_4^+ > K^+ > H^+ > Ca^{2+} > Mg^{2+}$. In practice, one would not actually use ammonium as an exchangeable ion because it is a pollutant. The pH of the H^+ solutions was 2.1. Experimental work indicated that the zeolite does not degrade appreciably until the pH is less than 2.

TABLE 10
Effect of Exchangeable Ions

	Counterion					
	NH_4^+	Na^+	H^+	Ca^{2+}	K^+	Mg^{2+}
Type of zeolite	Pb^{2+} Loading (meq/g)					
Chabazite:						
Bowie, AZ	1.07	1.07	0.3	0.41	0.59	0.23
Christmas, AZ	0.96	0.80	0.16	0.32	0.53	0.27
Clinoptilolite:						
Buckhorn, NM	0.97	1.0	0.36	0.27	1.0	0.34
Creede, CO	0.73	0.58	0.25	0.15	0.58	0.26
Hector, CA	0.75	0.81	0.39	0.29	0.67	0.24
Sheaville, OR	0.93	0.88	0.43	0.21	0.79	0.42
Erionite:						
Pine Valley, NV	1.0	1.03	0.49	0.48	1.03	0.092
Mordenite:						
Lovelock, NV	0.60	0.27	0.13	0.13	0.25	0.14
Union Pass, AZ	0.47	0.42	0.25	0.16	0.25	0.19
Phillipsite:						
Pine Valley, NV	0.92	0.99	0.55	0.24	0.92	0.32

Copper Mine Wastewater

Six columns were set up, each containing 10 g of untreated Owyhee County, ID, clinoptilolite to test metal removal from the Rio Tinto copper mine wastewater on a bench scale. One 1000 mL sample of the filtered wastewater (pH 2.62) was passed successsively through the columns at a volume flow rate of 1 mL/min (or 1.3 cm/min linear flow rate). The effluent solution from column 1 became the head solution for column 2 and so on for a total of 30 columns (each column was used five times). Each time the solution was passed through a column, the column was stripped with 500 mL of 3% NaCl to complete one cycle. After five cycles through the six-column train, no additional purification of the wastewater could be detected so the test was terminated. Based on this research, 1 kg of zeolite should effectively treat at least 3.33 L of the wastewater.

The results of the bench-scale column tests are shown in Figs. 2A and 2B and Table 11. The figures show how many parts-per-million of each metal were removed during each pass of the sample through a zeolite column. Figures 2A and 2B indicate that relatively more Al^{3+} and Fe^{3+}, the only trivalent ions, were removed during each cycle as compared to the divalent ions. This observation is consistent with ion-exchange theory which states that zeolites will have the highest affinity for trivalent ions followed by divalent and monovalent ions, respectively (*7*). Only a small amount of metal ions was removed during each cycle due to the presence of calcium in the feedwater which was preferentially taken up by the zeolite. This is unfortunate because there is less room in the zeolite for the metal ions, and the presence of calcium is needed by aquatic life (*8*). Calcium was almost completely removed (<3 ppm). Elution with 3% NaCl worked very well with all the metal ions being removed.

A larger scale experiment was conducted with a 20.3 cm by 91.4 cm column and a volume flow rate of about 8.3 mL/min (0.026 cm/min linear flow rate). The results of the larger scale test are shown in Table 12. These results are similar to the bench-scale test results except that the effluent zinc concentration was much higher, although still below EPA drinking water standards. In both experiments, concentrations of all the metals except nickel and manganese were reduced to below drinking water levels, and the capacity of the zeolite for all ions combined was 0.40 meq/g.

Simulated Berkeley Pit Water

To test the synthetic Berkeley Pit water, 13 columns were set up, each containing 17 g of Mudhill, CA, clinoptilolite. One 500 mL sample of synthetic Berkeley Pit water (pH 1.85) was passed successively through the columns at a volume flow rate of 1 mL/min (1.3 cm/min linear flow

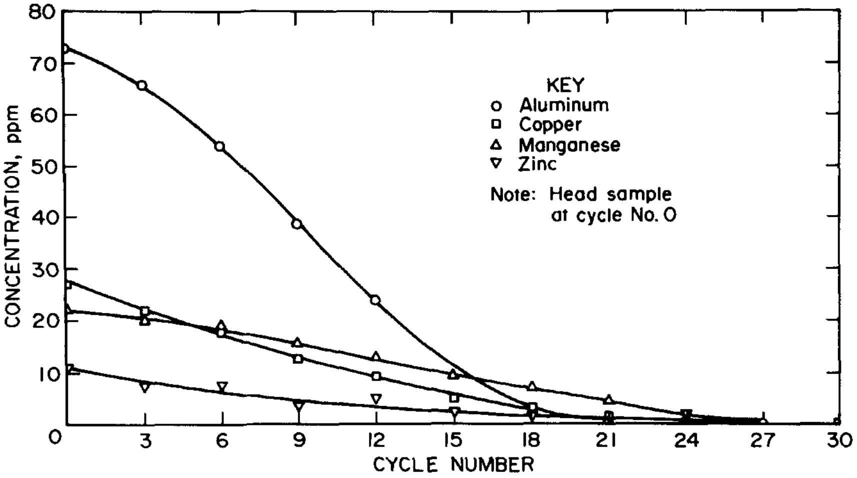

FIG. 2A. Results of bench-scale column tests of copper mine wastewater.

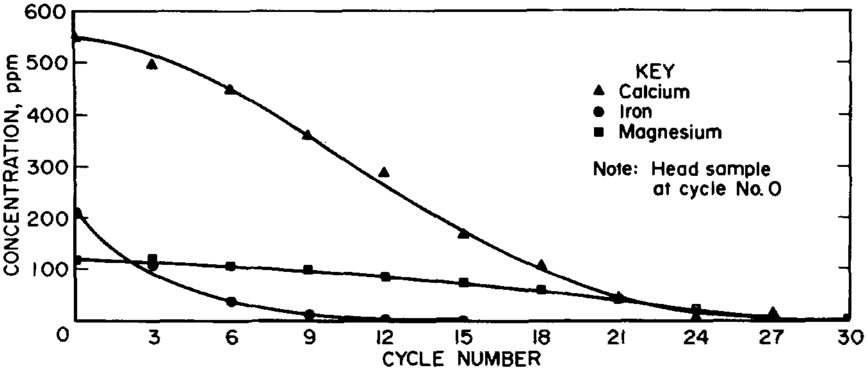

FIG. 2B. Results of bench-scale column tests of copper mine wastewater.

rate). The tail solution from column 1 became the head solution for column 2 and so on for all 13 columns (13 stages).

The results of the bench-scale test are shown in Table 13. The experiment was discontinued after 13 stages because no appreciable change in solution composition was observed in the latter stages due to competition from the high levels of sodium that built up from exchange in the earlier stages. Most of the aluminum, copper, and iron were removed. However, unacceptable amounts of manganese and zinc remained. When the concentra-

TABLE 11

Head and Effluent Analysis of Bench-scale Column Test for the Rio Tinto Copper Mine Wastewater

Ion	Head (mg/L)	Effluent (mg/L)
Al^{3+}	73	<1
Ca^{2+}	550	5.0
Co^{2+}	1.4	0.014
Cu^{2+}	27	0.05
Fe^{3+}	210	<0.05
Mg^{2+}	120	3.7
Mn^{2+}	22	0.35
Na^{+}	36	1600
Ni^{2+}	0.43	0.017
Zn^{2+}	11	0.08
pH	2.62	5.14

tion of metals is very high, as in the case for this wastewater, the amount of sodium exchanged from the zeolite builds to such a high level that no more exchange can take place. Here, even though the water quality was improved considerably, metal contaminants were not completely removed using this method alone.

TABLE 12

Head and Tail Analysis of Larger Scale Column Test for the Rio Tinto Copper Mine Wastewater

Ion	Head (mg/L)	Tail (mg/L)
Al^{3+}	73	<1
Ca^{2+}	550	<3
Co^{2+}	1.4	<0.02
Cu^{2+}	27	<0.6
Fe^{3+}	210	<0.5
Mg^{2+}	130	1.3
Mn^{2+}	22	0.25
Na^{+}	36	720
$Ni;^{2+}$	0.43	0.05
Pb^{2+}	1.4	0.004
Sr^{2+}	0.67	<0.01
Zn^{2+}	11	4.8

TABLE 13
Head and Effluent Analysis of Bench-scale Column Test for Synthetic Berkeley Pit Water

Ion	Head (mg/L)	Tail (mg/L)
Al	180	<3
Ca	530	290
Cd	2.9	0.56
Cu	180	<0.6
Fe	750	<0.5
Mg	230	150
Mn	140	30
Na	79	1700
Zn	380	17

SUMMARY AND CONCLUSIONS

1. Phillipsite had the best combination of high strength, high capacity, and high density.
2. The zeolites picked up lead regardless of the calcium or sodium concentration in the water.
3. Pretreatment with sodium enhances the capacity of the zeolite because sodium is less tightly held than divalent counterions.
4. The ions were concentrated by a factor of 30 during the eluting step.
5. When treating real wastewaters (such as the copper mine wastewater), the calcium content interferes with the uptake of metal ions and greatly increases the amount of zeolite needed to treat a given volume of wastewater.

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