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REMOVAL OF HEAVY METALS AND OTHER CATIONS FROM WASTEWATER 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-two zeolites were analyzed by X-ray diffraction and inductively coupled plasma analysis (ICP). These included clinoptilolite, mordenite, chabazite, erionite, and phillipsite. The zeolites were primarily in the sodium or calcium form, but potassium and magnesium counter ions were also present. Bulk densities of a sized fraction (minus 40, plus 65 mesh) varied from 0.48 to 0.93 g/cc. Heavy metal ion exchange loading values on two clinoptilolites ranged from 1.6 meq/g for lead to 0 meq/g for mercury in single ion tests. The selectivity series was determined to be

$$Pb>Cd>Cs>Cu(II)>Co(II)>Cr(III)>Zn>Ni(II)>Hg(II).$$

Sodium was the most effective exchangeable ion for ion 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. Aluminum, Fe(III), Cu(II), and Zn in the copper mine wastewater were removed to below drinking water standards, but Mn(II) and Ni(II) were not. Calcium and NH_4 were absorbed preferentially to all heavy metal cations except Pb. Adsorbed heavy metals were eluted from zeolites with 3-pct 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 most 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 both costly and hazardous to dispose of; (2) at around 4° C, the precipitation layer in settling ponds undergoes an inversion; (3) it may not produce an effluent sufficiently low in heavy metal content; and (4) the metal values are not directly recovered (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 waste water. As part of the program, naturally occurring zeolites are being explored as ion exchangers to remove the heavy metal ions with sodium ions.

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 framework 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).

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). The fundamental building block of the zeolites is a tetrahedron of four oxygen atoms surrounding a relatively small silicon or aluminum atom. The framework 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).

The objective of this investigation was to determine how efficient zeolites are at removing a variety of cations from 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 (5).

TEST MATERIALS AND SOLUTIONS

Zeolites

Extensive tests were performed on two zeolites: clinoptilolite from Owyhee County, ID, and clinoptilolite from Ash Meadows, NV. Complete chemical analyses of these zeolites are given in Table 2. Less extensive testing was done on several

TABLE 1
EPA Drinking Water Standards

Metal ion	Drinking water concentration, ppm
Cd................	0.01
Cr................	.05
Cu................	1
Fe................	.3
Mn................	.05
Ni................	.015
Pb................	.05
Zn................	5

TABLE 2
ICP Analyses of Owyhee County, ID, and Ash Meadows, NV, Clinoptilolite

Element	Owyhee Co., ID, ppm	Ash Meadows, NV, ppm
Al.....	6.5%	6.1%
As.....	320*	<300
Be.....	7.4	5.8
Bi.....	660*	730*
Ca.....	1.9%	0.72%
Cd.....	35	39
Co.....	66	60
Cr.....	290	300
Cu.....	160	190
Fe.....	1.4%	0.67%
K......	1.0%	2.2%
La.....	290	210
Mg.....	0.61%	0.34%
Mn.....	0.13%	700
Mo.....	76*	52*
Na.....	1.1%	2.5%
Nb.....	200	150
Ni.....	240	220
P......	<1,000	<1,000
Pb.....	380	420
Sb.....	<300	330*
Si.....	33.5%	34.9%
Sn.....	250	190
Sr.....	340	240
Ti.....	0.12%	590
V......	120*	99*
W......	390*	410*
Y......	110	50
Zn.....	730	630
Zr.....	430	170*

*Near detection limit.

other types of zeolites, such as phillipsite, erionite, chabazite, mordenite, and a commercial cat litter. Table 3 contains results from ICP and X-ray diffraction for each zeolite tested. The zeolites were used as received, except that some had to be ground to the proper size of minus 20 plus 60 mesh.

Simulated Wastewater Solutions

In acid mine drainage, the metal ions are predominantly present in the sulfate form, however, sulfates are generally difficult to dissolve. Therefore, other forms were chosen for making simulated wastewater solutions. Cadmium, chromium, nickel, and zinc solutions were made from chlorides except for lead, which was made from lead acetate or lead nitrate, and cobalt and copper, which were used in the sulfate form. These solutions were at ambient temperature and a natural pH of 5 - 7. A 3 pct sodium chloride solution was used to elute the metal ions from the loaded zeolites.

Mine Waste Stream

Wastewater was obtained from an abandoned copper mine located in northeastern Nevada. The wastewater had a pH of 2.62 and contained, in parts per million, 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

Bulk Density

Bulk density and loading values must be considered when selecting a zeolite based on performance at the lowest possible cost. As zeolite capacity is measured per unit weight, bulk density is important for process design. Table 4 shows the measured bulk density of zeolite samples ground to minus 42 plus 65 mesh. Clinoptilolite and mordenite, for which there were several samples, showed a wide range of bulk densities.

Shake Test

For the shake test, 1 g of Owyhee County, ID, clinoptilolite (minus 10 plus 50 mesh) was placed in each of three 250-mL Erlenmeyer flasks. Then, either 25, 50, or 100 mL of a 0.04 N lead acetate solution was added to each flask. The flasks were vigorously shaken for 20 hours. Cation uptakes were calculated from solution analyses done by ICP which has a detection limit of 1 ppm ±0.1. The results are shown in Table 5. Order of efficiency is as follows:

phillipsite>chabazite>erionite>clinoptilolite>mordenite.

This correlates with the corresponding Si/Al ratios shown in Figure 1. If all other factors are equal, a lower Si/Al ratio means a higher zeolite capacity (6). Maximum substitution of Al^{3+} for Si^{4+} results in a Si/Al ratio of 1.

TABLE 3
Zeolite X-ray Diffraction and ICP Analyses

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 Minor: 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
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 4
Zeolite Bulk Density (minus 42 plus 65 mesh)

Type zeolite	Location	Bulk density, g/cc
Chabazite.......	Bowie, AZ..................	0.59
	Christmas, AZ..............	.63
Clinoptilolite..	Death Valley Junction, CA..	.93
	Ash Meadows, NV............	.91
	Mud Hill, CA...............	.88
	Mountain Green, UT.........	.88
	Creede, CO.................	.82
	Fish Creek Mountains, NV...	.87
	Barstow, CA................	.78
	Hector, CA.................	.75
	Sweetwater, WY.............	.75
	Sheaville, OR..............	.66
	Buckhorn, NM...............	.64
	Owyhee County, ID..........	.53
	Castle Creek, ID...........	.48
Erionite........	Pine Valley, NV............	.60
	Shoshone, CA...............	.63
Mordenite.......	Middlegate, NV.............	.46
	Cat litter.................	.48
	Lovelock, NV...............	.64
	Union Pass, AZ.............	.90
Phillipsite.....	Pine Valley, NV............	.67

TABLE 5
Loading Values of Zeolites for Lead

Material tested	Volume of 0.04N solution, mL	Milliequivalents cation/ gram zeolite
Chabazite:		
Bowie, AZ..........	25	0.91
	50	1.35
	100	1.64
Clinoptilolite:		
Ash Meadows, NV....	25	.68
	50	.87
	100	1.06
Barstow, CA........	25	.80
	50	1.06
	100	1.25
Buckhorn, NM.......	25	.51
	50	.78
	100	.97
Castle Creek, ID...	25	.54
	50	.89
	100	1.06

(continued on next page)

TABLE 5
continued

Material tested	Volume of 0.04N solution, mL	Milliequivalents cation/ gram zeolite
Creede, CO.........	25	.43
	50	.48
	100	.58
Death Valley, CA...	25	.52
	50	.82
	100	1.06
Fish Creek Mtns, NV	25	.38
	50	.48
	100	.58
Hector, CA.........	25	.95
	50	1.30
	100	1.54
Mtn. Green, UT.....	25	.70
	50	.92
	100	1.06
Sheaville, OR......	25	.50
	50	.73
	100	.97
Mudhill, CA........	25	.77
	50	1.01
	100	1.16
Sweetwater, WY.....	25	.82
	50	1.11
	100	1.25
Oreana, ID.........	25	.51
	50	.63
	100	.77
Erionite:		
Pine Valley, NV....	25	0.54
	50	1.04
	100	1.54
Shoshone, CA.......	25	.54
	50	1.06
	100	1.25
Mordenite:		
Middlegate, NV.....	25	.36
	50	.53
	100	.58
Lovelock, NV.......	25	.27
	50	.34
	100	.39
Phillipsite:		
Pine Valley, NV....	25	.55
	50	1.06
	100	1.79

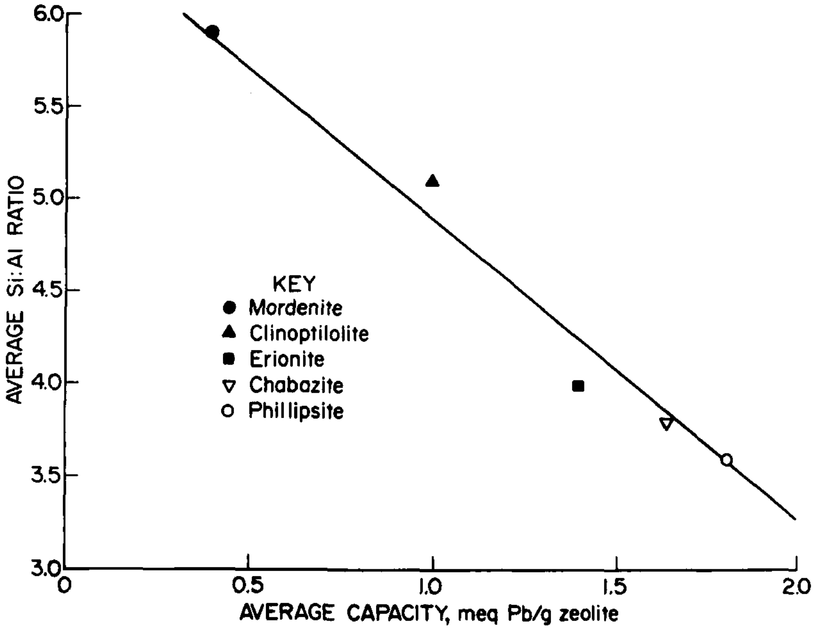

Fig. 1. Correlation between lead capacity and Si/Al ratio.

Column Tests

All column tests were done using 30-cm by 1.0-cm glass columns (95 pct filled with zeolite) topped by a 1-L reservoir. Loading tests were done by running 1 L of a 0.1 M solution containing the ion in question through the column. From ICP analysis of the head and tail solutions, the uptake was calculated. In all cases the flow rate was maintained at 1 mL/min to eliminate flow rate as a variable. All tests were done by gravity flow.

The loading values of the Owyhee County, ID, clinoptilolite for various metals are shown in Table 6. The loading values vary widely. The resulting selectivity series is

Pb>Cd>Cs>Cu(II)>Co(II)>Cr(III)>Zn>Ni(II)>Hg(II).

To test the effect of competing cations on zeolite loading, a solution containing 10 ppm of metal ion and 50 ppm of the competing ion was passed through a column of Owyhee County, ID, clinoptilolite. In subsequent tests the concentration of the competing ion was raised, while the metal ion remained at 10 ppm, until the tail analysis revealed that the metal ion was not being completely removed. Table 7 shows at what concentration each

TABLE 6
Loading Values of Owyhee County, ID, Clinoptilolite

Metal ion	Loading value meq/g
Cd^{2+}	1.2
Co^{2+}	.71
Cr^{3+}	.32
Cs^{+}	.95
Cu^{2+}	.82
Hg^{2+}	0.00
Ni^{2+}	.24
Pb^{2+}	1.6
Zn^{2+}	.25

TABLE 7
Results of Competing Ion Tests Which Show at What Concentration the Competing Ion Begins to Affect the Uptake of the Metal Ions at a Concentration of 10 ppm, Owyhee County, ID, Clinoptilolite

	Competing ions, ppm		
	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

competing ion began to affect the uptake of the metal ion. Nickel uptake was affected by low concentrations of calcium, sodium, and ammonia, while concentrations of 1,500 ppm Na^{+} and Ca^{+} had no effect on the uptake of lead.

A series of tests was performed to determine if elution is possible and if the concentration of metal ions could be increased in the eluate relative to the head solution. Three liters of water containing 10 ppm metal ion were put through each column containing Owyhee County, ID, clinoptilolite. Then, 100 mL of 3-pct NaCl solution was passed through the column. The elution was considered successful if all the metal going onto the column during loading came off during elution. Elution flow rate was 1 mL/min. Cadmium, Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} were totally eluted from the column. In the same test for lead, only 50 pct was eluted.

Each column was tested for between 27 and 37 cycles. A cycle was defined as the combination of one loading and one eluting step. Elution was complete and consistent for Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}. Lead behaved more erratically with as little as 40 pct elution in some runs and 300 pct in others. Since the zeolite was not changed, it was possible that the lead that did not come off during one elution could come off during a later one. In an overall mass balance, 95 pct of the loaded lead was recovered in the eluate. Chromium could not be eluted from the column with 3-pct NaCl solution, and as a result, after only a few cycles the column was exhausted. Chromium, at low concentrations, forms either a polynuclear complex or a hydrous oxide colloid at pH 5 (8). These are positively charged so they were picked up by the zeolite, but could only be removed using alkaline hydrogen peroxide at pH 11.

The zeolite was not successful at removing mercury from water because $HgCl_2$ does not disassociate appreciably based on the stability constants of the mercury-chloride system (9). The zeolite will not pick up an uncharged molecule.

Table 8 shows the loading values of Ash Meadows, NV, clinoptilolite for several cations. The test was conducted in the same manner as for Table 6. Although the zeolite behaved very similarly to the Owyhee County, ID, clinoptilolite, the loading values for Ash Meadows, NV, are about 40 pct lower. However, because the density of Ash Meadows, NV, clinoptilolite is about 40 pct higher, the performance of the two zeolites on a volume basis is the same.

Pretreatment

Pretreatment tests were done by first passing 1/2 L portions of the exchangeable ion (3 pct) through the column to displace the existing exchangeable ions. The zeolite was completely converted based on a mass balance calculation. Then, a solution containing 3,000 ppm lead was run through the column. The results of the exchangeable ion tests are shown in Table 9. Based on the data, the best exchangeable ions for lead uptake are ammonium ion and sodium, while the worst is magnesium. In order from best to worst the series is Na^{+}'NH_4^{+}>K^{+}>H^{+}>Ca^{2+}>Mg^{2+}. The pH of the H^{+} solutions was 2.1. Experimental work indicated that the zeolite

TABLE 8
Loading Values of Ash Meadows,
NV, Clinoptilolite

Metal ion	Capacity, meq/g
Cd	0.78
Co	.46
Cu	.52
Ni	.13
Pb	1.1
Zn	.15

TABLE 9
Effect of Pretreatment on Owyhee County, ID, Clinoptilolite

Type zeolite	Pb loading, meq/g counter ion					
	NH_4^+	Na^+	H^+	Ca^{2+}	K^+	Mg^{2+}
Chabazite:						
Bowie, AZ......	1.07	1.07	0.3	0.41	0.59	0.23
Christmas, AZ..	.96	.80	.16	.32	.53	.27
Clinoptilolite:						
Buckhorn, NM...	.97	1.0	.36	.27	1.0	.34
Creede, CO.....	.73	.58	.25	.15	.58	.26
Hector, CA.....	.75	.81	.39	.29	.67	.24
Sheaville, OR..	.93	.88	.43	.21	.79	.42
Erionite:						
Pine Valley, NV	1.0	1.03	.49	.48	1.03	.092
Mordenite:						
Lovelock, NV...	.60	.27	.13	.13	.25	.14
Union Pass, AZ.	.47	.42	.25	.16	.25	.19
Phillipsite:						
Pine Valley, NV	.92	.99	.55	.24	.92	.32

does not degrade appreciably until the pH is less than 2. The monovalent ions, except for H^+, worked better than the divalent ions. Of course, in practice, one would not actually use ammonium as an exchangeable ion because it is a pollutant.

Breakthrough Curves

Tests to determine breakthrough were done by gravity flow of a 112-ppm lead solution through a 30 x 10 cm (95 pct filled with zeolite) column at a flow rate of approximately 1 mL/min. Breakthrough curves for lead are shown in Figure 2. In each case, the curve is quite sharp which is good because it allows for maximum utilization of the zeolite. Analysis of the effluents before breakthrough shows the column bleed to be less than 0.03 ppm in each case. This level is below the drinking water standard of 0.05 ppm. The total loading of the Middlegate, NV, mordenite is 0.77 meq/g, for the cat litter 0.73 meq/g, and for the Owyhee County, ID, clinoptilolite 1.56 meq/g.

Copper Mine Wastewater

To test the copper mine wastewater, 30 columns (30 x 1 cm) were set up, each containing 10 g (1 x 28 cm bed) of untreated Owyhee County, ID, clinoptilolite (bench scale). One 1-L sample of filtered wastewater (pH 2.62) was passed successively through the columns at a flow rate of 1 mL/min or 1.3 cm/min. The tail solution from column 1 became the head solution for column 2 and so on for a total of 30 columns. Each time the solution had passed through a column, the column was eluted with 1/2 L of 3-pct NaCl to complete one cycle. After 30 cycles the changes in

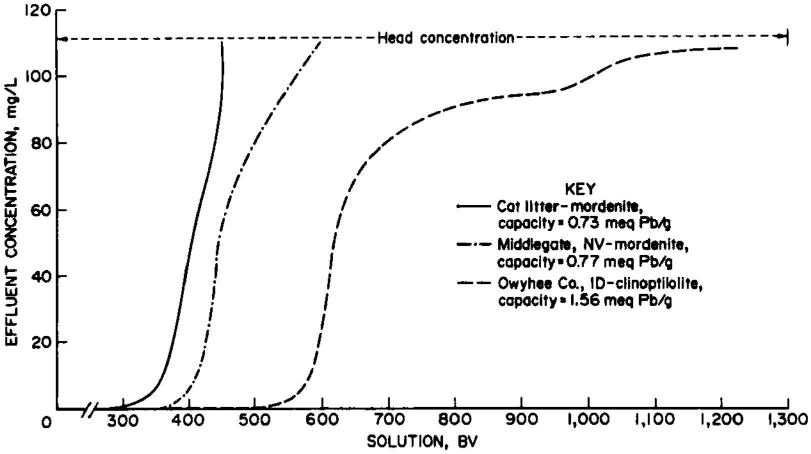

Fig. 2. Lead breakthrough curves.

impurity concentrations in the tail sample from the previous cycle was insignificant. Based on this work, it was calculated that 25 lb of zeolite should effectively treat 10 gal of the wastewater. This was tested on a larger scale with an 8-in by 36-in column (zeolite bed 8 in by 30 in) and a flow rate of about 1/2 L per hour (0.026 cm/min). Both tests utilized the same number of bed volumes.

The results of the bench scale column tests are shown in Figure 3 and Table 10. Figure 3A indicates that relatively more Al^{3+} and Fe^{3+}, the only trivalent ions, were removed during each cycle as compared to the divalent ions. Only a small amount of metal ions were removed during each cycle due to the presence of calcium which is also taken up by the zeolite. This is unfortunate because there is less room in the zeolite for the metal ions and the removal of calcium is undesirable because of its affect on aquatic life (10). Calcium was eventually almost completely removed. However, even when calcium was decreased to <3 ppm, the zeolite did not remove the metal ions completely. This was probably due to the buildup of sodium in the solution. Elution with 3 pct NaCl worked very well with all the metal ions being removed. The results of the larger scale test are shown in Table 11. These results were similar to the bench scale test results except the effluent zinc concentration was much higher, although still below EPA drinking water standards. In both tests, concentrations of all the metals except nickel and manganese were reduced to below drinking water levels. In both tests the loading value of the zeolite for all ions combined was 0.40 meq/g.

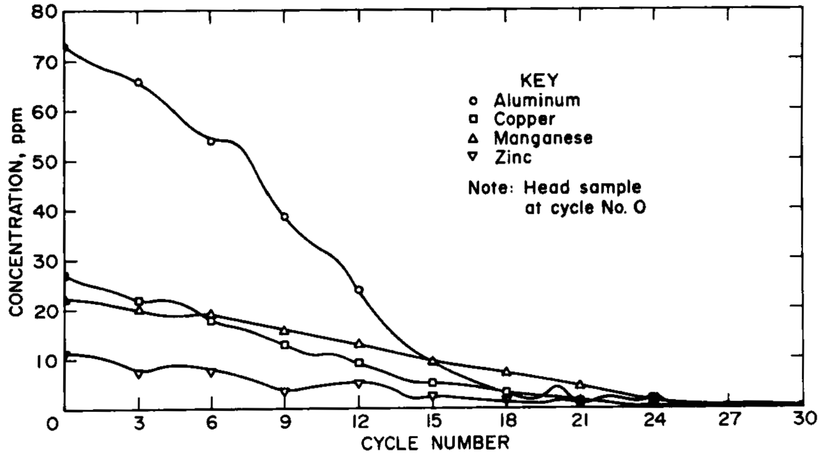

Fig. 3A. Results of bench-scale column tests of copper mine wastewater.

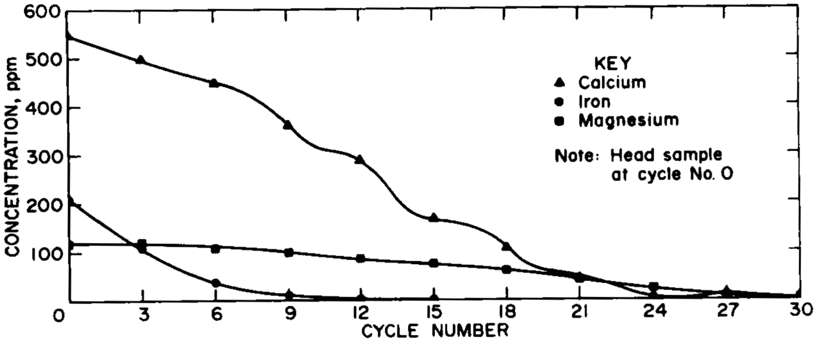

Fig. 3B. Results of bench-scale column tests of copper mine wastewater.

SUMMARY AND CONCLUSIONS

1. The clinoptilolite picked up lead regardless of how much calcium or sodium was present in the water.

2. Metals that do not form cations such as mercury were not picked up by the zeolite.

3. It was found that pretreatment with sodium enhances the capacity of the zeolite.

4. NaCl elution worked very well in all cases except for chromium ion.

5. The ions were concentrated by a factor of 30 during the eluting step.

6. When treating real wastewaters with clinoptilolite, 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.

TABLE 10
Head and Tail Analysis of
Bench-Scale Column Test for
the Copper Mine Wastewater

Ion	Head, ppm	Tail, ppm
Al^{3+}......	73	<1
Ca^{2+}......	550	5.0
Co^{2+}......	1.4	.014
Cu^{2+}......	27	.05
Fe^{3+}......	210	<.05
Mg^{2+}......	120	3.7
Mn^{2+}......	22	.35
Na^{+}.......	36	1,600
Ni^{2+}......	.43	.017
Zn^{2+}......	11	.08
pH........	2.62	5.14

TABLE 11
Head and Tail Analysis of
Larger Scale Column Test for
the Copper Mine Wastewater,
10 gal Wastewater Passed
Through 25 lb of Zeolite

Ion	Head, ppm	Tail, ppm
Al^{3+}......	73	<1
Ca^{2+}......	550	<3
Co^{2+}......	1.4	<.02
Cu^{2+}......	27	<.6
Fe^{3+}......	210	<.5
Mg^{2+}......	130	1.3
Mn^{2+}......	22	.25
Na^{+}.......	36	720
Ni^{2+}......	.43	.05
Zn^{2+}......	11	4.8

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