TREATMENT OF ACID MINE DRAINAGE USING NATURAL ZEOLITES

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ABSTRACT

Natural zeolites were investigated by the U.S. Bureau of Mines for treating acid mine drainage. Four clinoptilolite-rich and one phillipsite-rich samples were studied to determine exchange and regeneration characteristics. Based on 48-hr single-cation tests, the following general trend in effective cation-exchange capacity was determined for the tested zeolites: $Pb^{2+} > Ca^{2+} > Zn^{2+} > Mn^{2+} > Cu^{2+} > Cd^{2+} > Al^{3+} > Ni^{2+}$ (although the trend varied slightly between samples). The zeolites were used to treat acid mine drainage from the Rio Tinto mine, a closed Cu mine in northeastern Nevada. This water contains (mg/liter), 152 Al, 502 Ca, 101 Cu, 595 Fe, 80 Mn, and 61 Zn plus trace amounts of Cd, Co, and Ni. Clinoptilolite from Hector, California, required about 370 g for the complete removal of the metals from one liter at a flow rate of 5 bed volumes/hr (BV/hr). Phillipsite from Pine Valley, Nevada, required 403 g, whereas clinoptilolite from Buckhorn, New Mexico; Barstow, California; and Death Valley Junction, California; required 493, 490, and 546 g, respectively.

The uptake of metals from the Rio Tinto water in column tests was highly dependent on flow-rate. At a flow rate of 0.5 BV/hr, >99% of the Cu and 97% of the Zn were removed from solution. At a flow rate of 13 BV/hr, 65% of the Cu and 44% of the Zn were removed.

Four solutions were tested for the regeneration of the treated phillipsite. For 3% solutions of KCl, $MgCl_2$, NaCl, and $CaCl_2$ and flow rates of 4 BV/hr, NaCl regenerated the phillipsite (about 70%) followed by $CaCl_2$ and KCl. $MgCl_2$ was the least effective at regenerating the phillipsite (about 5%).

INTRODUCTION

Wastewaters from mineral processing operations commonly contain dissolved metals, which must be removed prior to discharge. Metal removal is often accomplished by precipitating hydrous oxides by the addition of CaO. Although this method is relatively simple and inexpensive, it has the following disadvantages: (1) it generates a large volume of sludge, which can be costly to dispose of; (2) at about 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 metal content; and (4) the metal values are generally not recoverable by ordinary techniques (Pahlman and Khalafalla, 1988). To help meet present and future, possibly more stringent, Environmental Protection Agency (EPA) and state requirements, the U.S. Bureau of Mines is investigating alternative methods for removing metals from wastewater. As part of the program, natural zeolites are being tested as ion exchangers to extract the metal ions.

Past research on metal exchange using zeolites has focused chiefly on identifying the selectivity series for various zeolites using laboratory solutions containing a limited number of cations. These studies have provided a basis for further research, but have not addressed the questions needed to utilize natural zeolites to treat actual wastewater, such as, the problems posed by multi-ion systems. As pointed out by Leppert (1988), such research would be very useful.

Acid mine drainage (AMD) refers to wastewater that originates from the leaching of sulfide minerals from metal ore bodies. These sulfide minerals, in particular Fe sulfides, such as pyrite, pyrrhotite, and marcasite, interact with air and water to form mineral acidity and dissolved sulfate salts. The pH of these waste streams is usually quite low (pH ≤ 2), however, some streams may be at or near neutral pH. Typically, these streams contain high concentrations of Al^{3+}, Cu^{2+}, $Fe^{2+/3+}$, Mn^{2+}, Zn^{2+}, and other metals, depending on the source minerals that have been oxidized (Beszedits and Netzer, 1986).

The objective of the present investigation was to determine the practicality of using natural clinoptilolite or phillipsite to treat AMD waste streams.

MATERIALS AND METHODS

Zeolites

Tests were conducted on five zeolite-rich tuffs from the western United States: clinoptilolite, Hector, California; phillipsite, Pine Valley, Nevada; clinoptilolite, Death Valley Junction, California; clinoptilolite, Barstow, California; clinoptilolite, Buckhorn, New Mexico. These zeolites were selected from a group of 30 zeolites on which several preliminary tests had been made (Zamzow and Murphy, 1992). These five samples exhibit-

ed superior physical integrity and/or cation-exchange capacity compared with the other 25 samples tested. The five zeolites were used as received at 20 x 60 mesh from Minerals Research, P.O. Box 591, Clarkson, New York 14430. Mineralogical and cation-exchange capacity information on similar reference zeolite samples from these localities were reported by Sheppard and Gude (1982).

Mine waste stream

AMD was obtained from the tailings pond of an abandoned Cu mine (Rio Tinto) located in northeastern Nevada. This wastewater had a pH of 2.2 and contained, in mg/liter, 152 Al, 502 Ca, 0.19 Cd, 4.8 Co, 101 Cu, 595 Fe, 24 K, 382 Mg, 80 Mn, 95 Na, 1.9 Ni, and 61 Zn.

Composition and mechanical properties

The mineral content of the five zeolite samples was identified by using X-ray diffraction analysis (Table 1). The Si:Al ratio was determined by inductively coupled plasma analysis (ICP) (Table 1). For Al determination, 0.5 g of zeolite was dissolved in a combination of 15 ml aqua regia and 1 ml HF. The solution was evaporated to dryness and diluting with dilute aqua regia to 100 ml before testing it on the ICP instrument. For Si analysis, 0.2 g of zeolite and 1.4 g of $LiBO_2$ were fused at 950°C for 15 min. The product was dissolved in 15 ml of dilute HNO_3 and brought to 100 ml with water before being tested on the ICP instrument.

Bulk density measurements were obtained by weighing 5 cm^3 of 42 x 65 mesh zeolite.

Relative attrition-resistance was measured by placing 25 g of dry zeolite (20 x 60 mesh) in a 250 ml volumetric flask with 75 ml of deionized water. The flask was shaken at 150 rpm for 1 hr in a Fisher Versa-Bath (water temperature = 20°C). The zeolite

Table 1. Mineralogical, chemical, and physical properties of zeolites used in this study.

Zeolite[1]	Location	X-ray diffraction mineralogy	Si/Al[3] ratio	Bulk[4] density (g/cm^3)	Attrition loss (wt. %)
Clinoptilolite	Barstow, California (27172)[2]	Major: Clinoptilolite Minor: Quartz	5.1	0.78	5.1
	Buckhorn, New Mexico (27082)	Major: Clinoptilolite	4.6	0.64	9.2
	Death Valley Junction, California (27162)	Major: Clinoptilolite	5.4	0.93	3.2
	Hector, California (27022)	Major: Clinoptilolite Intermediate: Quartz Minor: Mordenite	5.4	0.75	2.1
Phillipsite	Pine Valley, Nevada (27152)	Major: Phillipsite Trace: Quartz	3.6	0.67	3.8

[1]Zeolites obtained from Minerals Research, Clarkson, New York.
[2]Minerals Research reference sample numbers.
[3]Analysis of bulk sample.
[4]Samples were 42 x 65 mesh.

was then thoroughly dried at 85°C and screened through a 100-mesh screen. The weight of the <100-mesh fraction was used to calculate percent attrition.

Effective cation-exchange measurements

To determine an effective cation-exchange series for the five zeolites, shake tests were conducted. Two grams of each zeolite (20 x 60 mesh) were placed in an Erlenmeyer flask with 200 ml of single cation solution (Al, Ca, Cd, Cu, Mn, Ni, Pb, Zn). In AMD, the metals salts are predominately present in the sulfate form. We found that sulfates, except for $CuSO_4$, would not dissolve appreciably, and as a result, the single-cation solutions used were prepared from chlorides, except for copper, which was used in the sulfate form. All solutions were adjusted to pH 2 using sulfuric acid prior to the test, and the flasks were shaken at 150 rpm for 48 hr in a Fisher Versa Bath at 20°C.

The starting concentration was 350 mg/liter for all the cations except lead, which was 972 mg/liter. A higher lead concentration was used because at 350 mg/liter Pb was completely removed from the solution. Samples of solution from each flask were taken at 1 min, 10 min, 30 min, 4 hr, 24 hr, and 48 hr to measure how much exchange had taken place. The composition of all cation-exchange and regeneration solutions and effluents was measured by ICP spectroscopy.

Column tests

Flow rate greatly impacted the performance of the zeolites in column studies. In one test, 250 ml of Rio Tinto wastewater was added at flow rates of 25, 3.5 and 0.75 BV/hr through each of three 1.5 x 30 cm columns filled with clinoptilolite from Death Valley Junction. In a second test, 250 ml of Rio Tinto wastewater was passed through two 1.5 x 30 cm columns containing Hector clinopti-

lolite at flow rates of 13 and 0.5 BV/hr.

Rio Tinto wastewater

Thirty 1.5 x 30 cm columns containing about 35 g each of phillipsite were used to treat one liter of Rio Tinto wastewater. The wastewater was added to the first column, then the effluent was added to the second column, and so on until the same one liter of wastewater had passed through several columns. Each pass through the zeolite decreased the metal concentration in the wastewater, until drinking water standards were reached. This test was also made using the four clinoptilolite samples. In each test the wastewater was added to as many columns of clinoptilolite as necessary to reach the same metal concentrations in the effluent as that obtained using phillipsite. The flow rate throughout all the tests was 5 BV/hr.

Regeneration

For the regeneration tests, four 1.5 x 30 cm columns were each filled with 30 g of phillipsite. A 100-ml sample of Rio Tinto water was added to each column. Each column was eluted using 50 ml of a 3% by weight chloride solution of a test regeneration ion (i.e., Na, Ca, Mg, and K).

A 35-g sample of Hector clinoptilolite was exchanged with metals from a 250 ml sample of Rio Tinto in a 1.5 x 30 cm column. The clinoptilolite was regenerated using 34 ml of 20% by weight NaCl solution. One third of the eluate was allowed to stand overnight in the column to increase the contact time.

RESULTS AND DISCUSSION

Composition and mechanical properties

The starting zeolite samples contained only minor amounts of impurities (e.g.,

quartz). The Si/Al ratios for the clinoptilolite samples were within the accepted range for sedimentary clinoptilolite (Sheppard, 1971). The Pine Valley phillipsite, the Hector clinoptilolite, and the Barstow clinoptilolite contained chiefly sodium as the exchangeable cation. The Buckhorn clinoptilolite contained chiefly calcium, whereas, the Death Valley Junction clinoptilolite contained about equal amounts of potassium and sodium.

Bulk density, effective exchange capacity, and attrition resistance must be considered when selecting a zeolite based on performance at the lowest possible cost. Because exchange capacity is measured per unit of mass, bulk density is important for process design. Bulk density measurements are shown in Table 1. Clinoptilolite from Buckhorn, New Mexico, had the largest bulk density, whereas, clinoptilolite from Death Valley Junction, California, had the smallest bulk density of the five zeolite samples examined.

The results of the attrition test are shown in Table 1. Attrition resistance is important because low attrition resistance requires more zeolite to be added to makeup for loses, which increases the overall cost of the process. Also, fines produced by attrition may plug a column, thereby reducing the efficiency of the operation. The Buckhorn clinoptilolite produced the most fines in the attrition tests; hence, from a physical standpoint, this material would be less effective that the other four materials.

Effective cation-exchange measurements

Figures 1 and 2 show results for Zn and Cu exchange, respectively. Almost all ion exchange took place within the first 4 hr. At 48 hr, the degree of exchange was greater for Zn than for Cu for all five zeolites, therefore the zeolites have higher effective exchange capacities for Zn than for Cu. The results for the other metals were similar to those for Cu
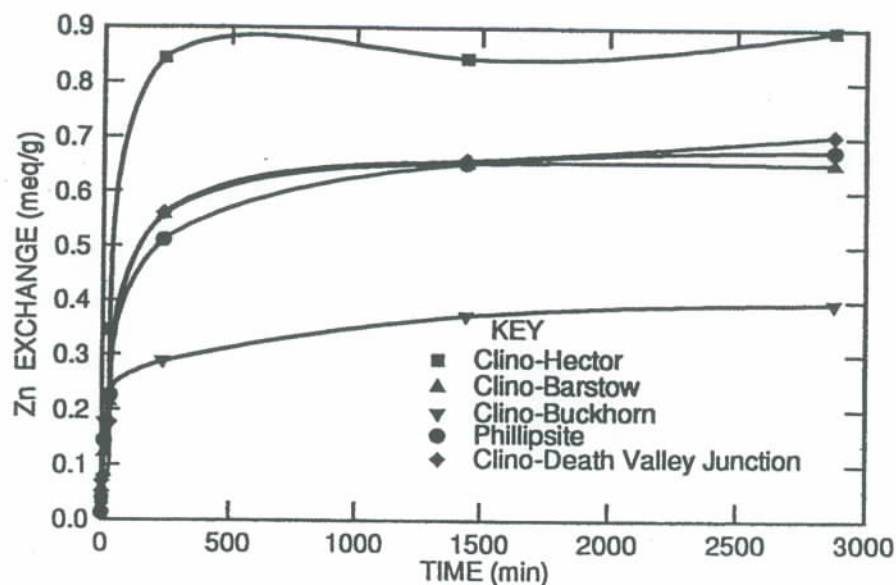
Figure 1. Amount of Zn exchanged (meq/g) from simulated Rio Tinto waste-water onto zeolite sites vs. time (min) during test using 2 g of zeolite and 200 ml of 350 ppm zinc solution shaken at 150 rpm for 48 hr.
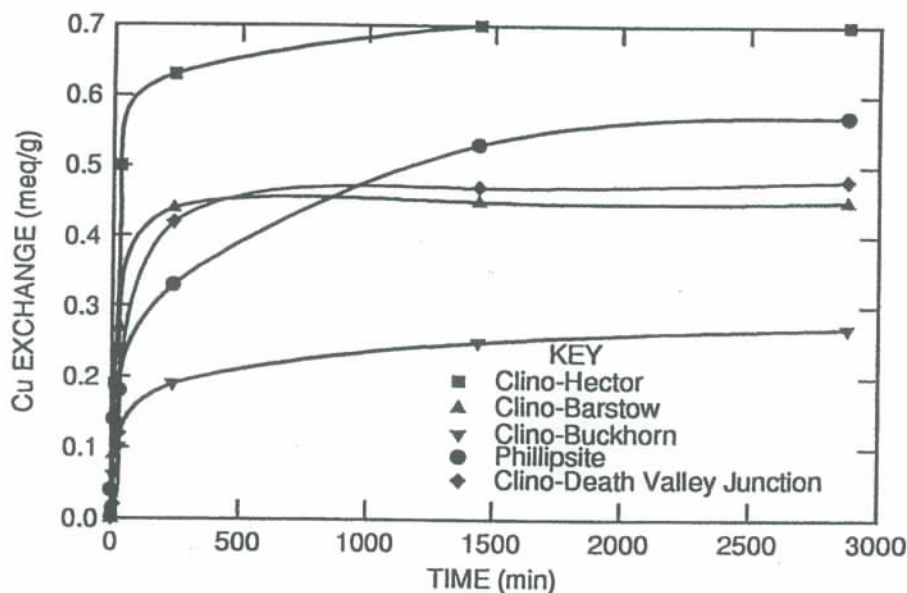

Figure 2. Amount of Cu exchanged (meq/g) from simulated Rio Tinto wastewater onto zeolite sites vs. time (min) during test using 2 g of zeolite and 200 ml of 350 ppm copper solution shaken at 150 rpm for 48 hr.

Table 2. Zeolite effective cation-exchange capacity (meq/g) using 350 mg/liter single cation solutions.

Zeolite	Al	Ca	Cd	Cu	Mn	Ni	Pb[1]	Zn
Barstow[2]	0.34	0.70	0.42	0.45	0.50	0.24	0.90	0.65
Buckhorn[2]	0.20	0.36	0.30	0.27	0.38	0.20	0.80	0.65
Hector[2]	0.26	1.1	0.50	0.70	0.80	0.31	0.80	0.90
Death Valley Junction[2]	0.34	0.70	0.44	0.49	0.65	0.14	0.90	0.70
Pine Valley[3]	0.28	0.80	0.49	0.55	0.50	0.14	0.95	0.70

[1]972 mg Pb/liter starting solution.
[2]Clinoptilolite.
[3]Phillipsite.

and Zn. Table 2 shows the effective cation-exchange capacities of the five zeolites at 48 hr for each metal. Based on these results, the following general trend for effective exchange-capacity series was obtained (although the trend varied slightly between samples): Pb > Ca > Zn > Mn > Cu > Cd > Al > Ni. This sequence is similar to the selectivity sequence of clinoptilolite established for divalent metal cations: $Pb^{2+} \approx Ba^{2+} >> Cu, Zn, Cd$ (Semmens and Seyfarth, 1978).

Column tests

The results of the flow-rate tests (Table 3) show that longer contact times were necessary to achieve maximum exchange. This is unfortunate because the longer the contact time required, the more zeolite needed to treat a AMD waste stream at a given flow rate. More zeolite adds cost to the process not just for the zeolite, but also for additional or larger equipment (Breck, 1974).

Rio Tinto wastewater

The clinoptilolite from Hector required 370 g to achieve the same effluent levels (shown in Table 3) as were achieved using 403 g of phillipsite. The clinoptilolites from Buckhorn, Barstow, and Death Valley Junction required 493, 490, and 546 g, respectively to remove the metals from the wastewater. If, as for zeolites, the breakthrough curve is shallow, and thus leaves a large proportion of unused capacity at the breakthrough point, it would be more efficient to use two or more beds in series. In this manner, a new bed is introduced at the downstream end each time a completely spent bed upstream is removed from service for regeneration (Chemical Engineers Handbook, 1973).

The Cu, Fe, Mn, and Zn concentrations were reduced to less than drinking water standards, which are: 0.2 Al, 1 Cu, 0.3 Fe, 0.05 Mn, 5, and Zn mg/liter (Environmental Protection Agency, 1993). Apparently, not all of the Fe removal was due to ion exchange, because some precipitate was noted. The pH of the solution increased from 2.2 in the influent to about 6 in the final effluent solution. Ca was removed by the zeolite and replaced by Na, which may be a problem because if the metals are not completely removed, soft water exacerbates the effect of heavy metals on fish (Krenkel and Novotny, 1988). Additionally, calcium exchange uses up much of the capacity of the zeolite, which decreases the capacity for metals.

Table 3. Composition of effluent (mg/liter) from Rio Tinto wastewater after zeolite treatment.

Metal	Head	Effluent[1] 25 BV/hr	Effluent[1] 3.5 BV/hr	Effluent[1] 0.75 BV/hr	Effluent[2] 13 BV/hr	Effluent[2] 0.5 BV/hr	Effluent[3]
Al	152	126	124	122	137	53	<3.2
Ca	502	426	310	189	239	39	24
Cd	0.19	0.19	<0.14	<0.085	0.10	<0.10	<0.03
Co	4.8	4.3	3.5	3.4	3.3	1.6	<0.31
Cu	101	69	31	10	35	<0.36	<0.05
Fe	595	314	75	6	21	<0.13	<0.1
K	24						<14
Mg	382	338	333	321	307	226	144
Mn	80	68	54	40	54	14	<0.03
Na	95						1900
Ni	1.9						0.83
Zn	61	50	35	18	34	2	<0.96

[1]Clinoptilolite from Death Valley Junction, California, and 250 ml of Rio Tinto wastewater in a 1.5 x 30 cm column.

[2]Flow rate using clinoptilolite from Hector, California, and 250 ml of Rio Tinto wastewater in a 1.5 x 30 cm column.

[3]Composition of effluent after treatment using one of the following: 403 g of Pine Valley phillipsite, or 370 g, 490 g, 493 g, or 546 g of Hector, Barstow, Buckhorn, or Death Valley Junction clinoptilolite, respectively.

Regeneration

To determine if metals could be extracted from a sample of clinoptilolite from Hector, that had previously been treated with 250 ml of Rio Tinto wastewater, an EPA toxicity-characterization leaching procedure (TCLP) was performed on the clinoptilolite (Environmental Protection Agency, 1986). The test demonstrated that Cu, Mn, and Zn could be extracted at concentrations that exceed water-quality standards. Therefore, the possibility of regenerating treated zeolites, instead of simply discarding them, was explored.

NaCl solution removed the most metals from the phillipsite. CaCl$_2$ solution was comparable to NaCl solution, whereas MgCl$_2$ and KCl solutions removed hardly any metals. These results are shown in Table 4 for phillipsite.

An important part of elution is to achieve high concentrations of metals relative to the feed. In attempting to concentrate the metals by an arbitrary factor of ~7, Ca and Zn were completely eluted, but Cu, Mg, and Mn were not completely eluted by a 20% NaCl solution from Hector clinoptilolite (Table 5).

SUMMARY AND CONCLUSIONS

Based on the results of the shake tests, the five zeolite-rich tuffs tested displayed a high effective CEC for Pb, followed by a general trend in descending order for Ca, Zn,

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Table 4. Eluant compositions [mg/liter, (%)] using 50 ml of 3% solutions to treat phillipsite, Pine Valley, Nevada, previously treated with 100 ml of Rio Tinto wastewater.

Metal	NaCl	CaCl$_2$	KCl	MgCl$_2$
			Solutions	
Al	93 (31)	62 (20)	69 (23)	12 (4)
Ca	308 (31)	ND[1] (-)	178 (18)	8 (0.7)
Cu	25 (12)	15 (7)	12 (6)	0.3 (-)
Fe	0.2 (-)	0 (-)	0 (-)	0 (-)
Mg	71 (9)	80 (10)	35 (5)	ND[1] (-)
Mn	22 (14)	25 (16)	8 (5)	1.4 (1)
Zn	29 (24)	22 (18)	11 (9)	2 (2)

[1]Not detected

Table 5. Regeneration test using 35 g Hector, California, clinoptilolite that had been treated with Rio Tinto wastewater and 20 wt. % NaCl solution.

Metal	Exchanged[1] (mg/g)	Eluted[2] (mg/g)	Eluted (%)
Ca	3.3	3.3	100
Cu	0.63	0.46	73
Fe	2.4	0.94	39
Mg	0.69	0.29	42
Mn	0.40	0.31	79
Zn	0.29	0.29	100

[1]Exchanged onto zeolite sites from Rio Tinto wastewater.
[2]Removed from zeolite exchange sites by Na$^+$.

Mn, Cu, Cd, Al, and Ni. In general, little Pb is present in AMD, but usually high concentrations of Zn, Mn, and Cu are present, which are high on the effective CEC trend for these zeolites. For appreciable exchange to take place in a column, a long contact time is required, which would probably restrict this technique to small seeps vs. a large flow or pit. With sufficient contact time, however, the zeolites will reduce the concentrations of cations in AMD to or less than drinking water standards and simultaneously raise the pH to near neutral. Using NaCl solutions, the zeolite can be regenerated to obtain a concentrated eluate.

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