AMD CLEANUP USING NATURAL ZEOLITES[1]

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Abstract: The U.S. Bureau of Mines is investigating the use of natural zeolites to remove metals from acid mine drainage (AMD). The loading characteristics of Al^{3+}, Ca^{2+}, Cu^{2+}, Fe^{2+}, H^{+}, Mg^{2+}, and Zn^{2+} were studied for samples of clinoptilolite from Barstow, CA, Buckhorn, NM, and Hector, CA. The relative order of cation selectivity was $Zn^{2+} > Ca^{2+}, Cu^{2+} > Fe^{2+} > H^{+} > Mg^{2+} > Al^{3+}$. The order of exchange capacity for the three zeolites was Hector > Barstow > Buckhorn, which corresponds to the Na content of the three zeolite samples. An acid mine drainage sample from the Rio Tinto Mine, an abandoned copper mine in northeastern Nevada, was used to measure the zeolites' cleanup potential. This water contained, in mg/L, 152 Al^{3+}, 502 Ca^{2+}, 101 Cu^{2+}, 595 $Fe^{2+/3+}$, 80 Mn^{2+}, and 61 Zn^{2+}. At an approximate flow rate of 4 mL/min (5 bed vol/h), 75% as much zeolite was required to clean the water to drinking water standards when the Hector material was used as compared with the zeolites from Buckhorn or Barstow. Zeolites were regenerated using 25% sodium chloride solutions. Loading and regeneration studies show no detectible degradation in the loading ability of the zeolites through 18 cycles.

Introduction

The U.S. Bureau of Mines is investigating alternate methods of treating water from mines producing acidic drainage (AMD). The water is characterized by metal sulfates that exceed State or Federal discharge limits (Bureau of Mines, 1975; Beszedits and Netzer, 1986). The acidity of the water originates from oxidation of iron sulfide minerals through a complex combination of chemical and bacterial action, primarily with pyrite, to form sulfuric acid. The acidic water leaches metal cations from the contacted minerals. AMD is a problem with both some modern mining operations and some abandoned mines. The most common approach to treating AMD is lime addition to precipitate metals and neutralize acidity (Patterson, 1985). 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 is classified as hazardous, (2) at around 4° C, the precipitation layer in settling ponds undergoes an inversion that 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 lost (Pahlman and Khalafalla, 1988).

To help meet present and possibly more stringent future Environmental Protection Agency (EPA) and State requirements, naturally occurring zeolites are being explored as ion exchangers to exchange the metal ions with sodium ions. More than 30 distinct species of zeolite occur in nature, of which mordenite, clinoptilolite, ferrierite, chabazite, erionite, phillipsite, and analcime occur in sufficient quantity to be considered as viable mineral resources (Vaughan, 1978).

The objectives of this investigation are to define the cation exchange characteristics of natural zeolites and to determine their efficiency in cleaning up AMD waste streams. Since the goal is to reduce impurities to below drinking water standards, the EPA standards are included for reference in table 1.

Table 1. EPA drinking water standards.

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

Source: The Water Encyclopedia, 1970.

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Test Materials and Solutions

Zeolites

Tests were conducted on three natural zeolites[3] from two States in the Western United States:

Clinoptilolite, Hector, CA
Clinoptilolite, Barstow, CA
Clinoptilolite, Buckhorn, NM.

These zeolites were selected for further study from a field of 30 zeolites on which several preliminary tests were done (Zamzow and Murphy, 1992). They exhibited superior physical integrity and loading ability. The three zeolites were used as received at minus 20 plus 60 mesh.

Single-Ion Solutions

Test solutions were prepared from reagent grade chemicals using water purified by reverse osmosis. Solution concentrations were verified by inductively coupled plasma (ICP) spectrographic analysis.

Mine Wastewater

Wastewater was obtained from an abandoned copper mine (Rio Tinto) tailings pond in northeastern Nevada. This wastewater had a pH of 2.2. Table 2 shows its analysis.

Table 2.--Wastewater analysis, mg/L

Metal	Concentration
Al.	152
Ca.	502
Cd.	.19
Co.	4.8
Cu.	101
Fe.	595
K	24
Mg.	382
Mn.	80
Na.	95
Ni.	1.9
Zn.	61

Experimental Procedures

Composition and Mechanical Properties

Table 3 contains the results of X-ray diffraction and ICP analyses for the three zeolites. Exchangeable cation concentrations were converted to milliequivalents per gram (meq/g) for ease in making comparisons of loading capacities.

Attrition tests were done by placing 25 g of dry zeolite (minus 20-, plus 60-mesh) in a 250-mL volumetric flask with 75 mL of deionized water. The flask was shaken at 150 rpm for 1 h by a Fisher Versa-Bath[4]. The zeolite was then thoroughly dried and screened through a 100 mesh screen. The weight of the minus 100- mesh fraction was used to calculate the percent attrition.

[3]Zeolites were purchased from a commercial supplier.

[4]References to specific brand products do not imply endorsement by the Bureau of Mines.

Table 3.--Zeolite X-ray diffraction and ICP analyses

Location	Mineralogy (X-ray diffraction)			
Barstow, CA	Clinoptilolite>>quartz>mordenite.			
Buckhorn, NM	Clinoptilolite.			
Hector, CA	Clinoptilolite>quartz>mordenite.			
	Chemical analysis, meq/g			
	Na	K	C	Mg
Barstow, CA	1.17	0.31	0.65	0.34
Buckhorn, NM	.52	.25	1.20	.91
Hector, CA	1.52	.23	.34	.16

Breakthrough Profiles

Studies were performed using 30- by 1.0-cm glass columns at ambient temperature. Each column was loosely packed with approximately 35 g of zeolite. The columns were operated under flooded conditions using a reservoir containing 1 L of loading solution at the top of each column. The bottom outlets of the columns were fitted with control valves to regulate the flow rates of the effluent to 1 mL/min ($\approx$1.4 bed vol/h). Each column was loaded with a 0.02N sulfate solution of the test cation. A 0.02N solution of H_2SO_4 was used in the H^+ studies. These concentrations were chosen to represent some of the higher concentrations known to exist in AMD. For example, 0.02N H_2SO_4 is pH 1.8 and 0.02N Ca is 401 mg/L.

The column effluents were periodically measured for volume and pH and analyzed for Na^+ and test cation concentrations. As the test progressed, the test cation concentration in the effluent abruptly increased and approached that of the loading solution with a simultaneous drop in Na^+ concentration. The point where the test cation began to increase in concentration in the effluent was considered the breakthrough point. The effluent prior to breakthrough typically contained <1 mg/L of the test cation and 0.022N Na^+. The loading, in milliequivalents (meq), was determined from the volume of the effluent and the change in concentration from the 0.02N loading solution. The cation exchange capacity (meq/g) was then calculated based on grams of zeolite in the column.

Rio Tinto Wastewater

A 1.5- by 30-cm column containing zeolite from Hector, CA, was used to treat 1 L of Rio Tinto wastewater. The zeolite was discarded and fresh zeolite placed in the column. The effluent from the first pass was treated with the fresh zeolite. The zeolite was again discarded, and replaced with fresh, and the effluent from the second pass was treated. This sequence was repeated 10 more times for a total of 12 treatments of 1 L of Rio Tinto wastewater. The total weight of zeolite used in the 12 columns was recorded. This test was repeated using each of the clinoptilolites. Treatment was continued until the effluent exceeded or matched that obtained in the first test. The flow rate throughout all the tests was about 5 bed vol/h.

Recycle

Multiple cycle tests were done by loading a 35-g sample of Hector clinoptilolite with metals from a 250-mL sample of Rio Tinto in a 1.5- by 30-cm column at a flow rate of 5 bed vol/h. The zeolite was regenerated using 34 mL of 25% NaCl solution. This was accomplished by flooding the column and allowing it to stand for 1/2 h before draining and reflooding. The final portion (approximately 7 mL) of eluate was allowed to stand overnight to increase the contact time. The zeolite was subjected to 18 loading and stripping cycles.

Results and Discussion

In single cation-solutions containing no competing cations, the breakthrough point is a measure of the affinity of the zeolite for that particular cation. The greater the loading prior to breakthrough, the greater the affinity. Table 4 summarizes the data for the breakthrough studies.

Table 4. Breakthrough values for three clinoptilolite zeolites, meq/g.

Ionic specie	Origin of zeolite		
	Barstow, CA	Buckhorn, NM	Hector, CA
Al^{3+}	0.15	0.05	0.25
Ca^{2+}	.65	.10	1.05
Cu^{2+}	.45	.28	.95
Fe^{2+}	.13	.18	.50
H^{+}	.28	.30	.36
Mg^{2+}	0	0	.35
Zn^{2+}	.45	.20	1.20

Data from table 4 was used to predict the following orders of cation selectivity for a 0.02N single-cation solution:

Barstow: $Ca^{2+} > Cu^{2+}, Zn^{2+} > H^{+} > Al^{3+} > Fe^{2+} > Mg^{2+}$
Buckhorn: $H^{+} > Cu^{2+} > Zn^{2+} > Fe^{2+} > Al^{3+} > Ca^{2+} > Mg^{2+}$
Hector: $Zn^{2+} > Ca^{2+} > Cu^{2+} > Fe^{2+} > H^{+} > Mg^{2+} > Al^{3+}$

For the Barstow and Hector samples, the orders of selectivity indicate that, given equinormal concentrations, Ca^{2+} is preferred over most of the other tested cations. This means that, when dealing with AMD for which the concentration of Ca^{2+} is frequently greater than that of any other cation, enough exchange capacity will be needed to remove most of the Ca^{2+} before other cations will be able to successfully compete for exchange sites. The sequence for the Hector sample more accurately represents general selectivity since that sample contains few exchangeable cations other than Na^{+} (table 3). Previously published data, containing breakthrough profiles for each of the tests summarized in table 4, demonstrate that Na^{+} is the exchanged cation in these tests (Bremner and Schultze, 1993). The sequence for the Buckhorn sample, for example, includes competition of cations for sites already occupied by Ca^{2+}, a cation that is not readily displaced.

The order of zeolite capacity from table 4 is Hector > Barstow > Buckhorn. This is considered a general order because it holds for most of the cations: Al^{3+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, and Zn^{2+}. For Fe^{2+} and H^{+} the order is Hector > Buckhorn > Barstow, where the values for Barstow and Buckhorn zeolites are very similar and may be indistinguishable. The order Hector > Barstow > Buckhorn corresponds to the Na^{+} content in table 3 and is consistent with Na^{+} being the principal exchangeable cation.

Table 5 shows the percent loss for the zeolites due to attrition (Zamzow and Schultze, 1993). The rate of attrition is important because a high rate requires more zeolite makeup, which increases cost. Also, the fines produced through attrition will plug the column, thereby reducing the efficiency of the operation.

Table 5.--Attrition loss of clinoptilolite zeolites

Origin of zeolite	Percent loss
Barstow, CA	5.1
Buckhorn, NM	9.2
Hector, CA	2.1

Results from tests to clean up the Rio Tinto wastewater demonstrate that the concentration of most cations can be decreased at least to drinking water standards (table 6). The clinoptilolite from Hector, CA, required 370 g to achieve the same effluent levels achieved using 490 g or 493 g of the clinoptilolites from Buckhorn or Barstow, respectively. More of the clinoptilolites from Barstow or Buckhorn is needed because many of the exchange sites are already occupied by Ca (table 3), which is not easily displaced by the cations present in the wastewater. The tests were designed to obtain pure water rather than to optimize zeolite usage. Similar discharge compositions should be feasible using smaller quantities of zeolite if a countercurrent contact method is employed.

Table 6.--Metals removed from copper mine wastewater

Metal	Head, mg/L	Effluent, mg/L
Al	152	<3.2
Ca	502	24
Cd	.19	<.03
Co	4.8	<.31
Cu	101	<.05
Fe	595	<.1
K	24	<14
Mg	382	144
Mn	80	<.03
Na	95	1900
Ni	1.9	.83
Zn	61	<.96

Data from the recycle tests (fig. 1) demonstrate good recycle characteristics for zeolites. There is no measurable decrease in cation exchange through multiple loading and stripping cycles beyond some stabilization during the first few cycles. As predicted from single-cation studies, the majority of the exchange capacity is utilized by Ca^{2+}.

Conclusions

The above results demonstrate that clinoptilolites can remove metal cations commonly found in acid drainage wastewaters. Most cations can be reduced to meet drinking water standards. The extent of loading and the preference for one cation over another varies according to the ratios of Ca and Na present in the zeolite, with Na being more easily exchanged. Loaded zeolites can being regenerated using a NaCl solution, and multiple cycles of loading and stripping exhibit no deterioration of exchange capacity. Based on the research results, some site criteria have been established where zeolites would have a high probability of success in the field. Field tests are planned for the near future.

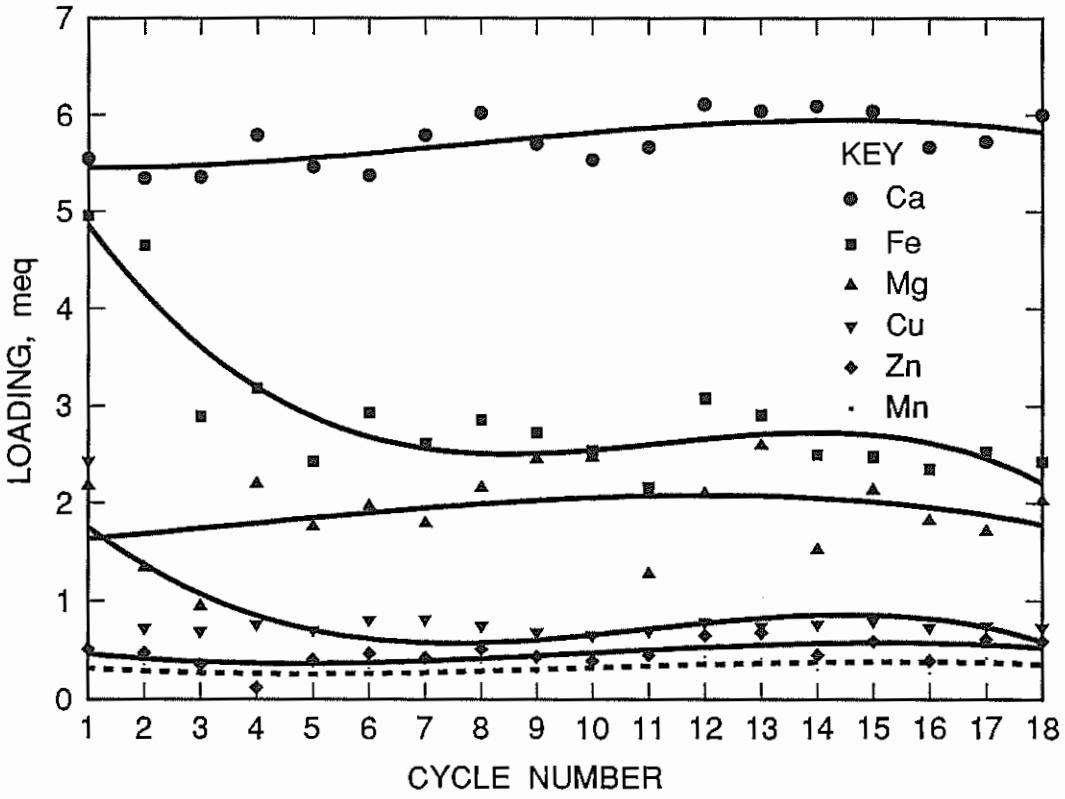

Figure 1. Effect of recycling on metals loading.

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