

ABILITY OF CLINOPTILOLITE-RICH TUFFS TO REMOVE METAL CATIONS COMMONLY FOUND IN ACIDIC DRAINAGE

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ABSTRACT

The loading characteristics of Al^{3+} , Ca^{2+} , Cu^{2+} , Fe^{2+} , H^+ , Mg^{2+} , and Zn^{2+} were studied on as-received samples of clinoptilolite-rich tuff from Barstow, California; Buckhorn, New Mexico; and Hector, California; as part of an effort to test natural zeolites for their ability to clean up acidic mine wastewaters. Each sample was loaded with a 0.02 N single-cation sulfate solution until breakthrough occurred, i.e., the point of an abrupt and continuous increase in cation concentration in the effluent. Using the breakthrough point for a cation as a measure of the zeolitic tuff's affinity for that particular cation, the relative order of affinity or take-up was: $Zn^{2+} > Ca^{2+}$, $Cu^{2+} > Fe^{2+} > H^+ > Mg^{2+} > Al^{3+}$. For the three zeolitic tuffs, the order of affinity (i.e., effective exchange capacity for the specified cations determined by such single-cation breakthrough curves) for each cation was: Hector > Barstow > Buckhorn, the same order as the Na content of the three untreated zeolitic tuffs. Analyses of effluent compositions during the loading process indicated that Na^+ was the principal cation exchanged from zeolitic sites. Zeolitic tuffs having a high ratio of Ca to Na were less efficient than others for wastewater clean up.

INTRODUCTION

The U.S. Bureau of Mines is investigating alternate methods of treating water from mines producing acid rock drainage (ARD). 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 the oxidation of iron sulfide minerals through a complex combination of chemical and bacterial action, primarily with pyrite, to form sulfuric acid (Bureau of Mines, 1975). The acidic water leaches metal cations from the contacted minerals. ARD is a problem in some modern mining operations and for some abandoned mines.

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The most common approach to treating ARD is the addition of lime to precipitate metals and neutralize acidity (Patterson, 1985). Some disadvantages of the lime treatment are: (1) the sludge produced is voluminous and difficult to dewater; (2) the sludge can be costly to dispose of, particularly if it is classified as a hazardous waste; (3) lime treatment may not lower metal concentrations sufficiently to meet water discharge standards; (4) the volume of sludge is increased by the precipitation of gypsum; and (5) all Fe must be oxidized before or during the addition of lime (Zamzow *et al.*, 1990). It is not unusual for a single coal mine to treat 1×10^6 gal (3.8×10^6 liter) of ARD per day. Treatment costs can be as much as \$500,000 each year, with the entire industry probably spending more than $\$1 \times 10^6$ each day (Ackman and Kleinmann, 1984).

Recently, zeolites have been considered as an alternative to lime treatment. The advantages of treating ARD with zeolites to remove heavy metals are: (1) zeolites are plentiful and inexpensive, (2) they possess cation-exchange characteristics, (3) they can be regenerated, and (4) they neutralize acidity. A major disadvantage of using zeolites to treat ARD is the increased exchange capacity required if cations such as Al^{3+} , Ca^{2+} , Fe^{2+} , and Mg^{2+} compete with more toxic cations such as Cu^{2+} and Zn^{2+} for exchange sites on the zeolite. The former set of cations are commonly present in ARD in relatively high concentrations and are known to compete at zeolite exchange sites with metals that must be removed before the water can be safely discharged (Bush *et al.*, 1993; Zamzow *et al.*, 1990).

A great deal of work has been carried out on the cation-exchange characteristics of zeolites and some excellent reviews have been published (e.g., Breck, 1974). Semmens (1983) and others have also discussed competition of cations for exchange sites. These reports, however, have focussed on equilibrium tests, which can require days or weeks of contact, unless multiple contacts with concentrated solutions are employed. Little information has been found that allows predictions to be made of the steady-state behavior of cations common to ARD.

The objective of the present study was to define the cation-exchange characteristics of three zeolitic tuffs by determining the order of affinity, i.e., the effective exchange capacity for the specified cations determined by single-cation breakthrough curves, for Al^{3+} , Ca^{2+} , Cu^{2+} , Fe^{2+} , H^+ , Mg^{2+} , and Zn^{2+} for three clinoptilolite-rich tuffs from different deposits. The order of cation affinity and the loading capacities at breakthrough were determined using single-cation breakthrough curves. Knowledge of the affinities, combined with chemical and mineralogical analyses of the natural zeolitic tuff, have provided

a basis for estimating the potential of these materials to treat acid mine drainage.

SAMPLE DESCRIPTION

All tests were made on 20 x 60 mesh (0.25 x 0.85 mm) samples received from Minerals Research, P.O. Box 591, Clarkson, New York 14430. X-ray diffraction analyses confirmed that the major mineral phase in all three samples was clinoptilolite. The sample from Barstow, California (Minerals Research reference zeolite number 27172), contained minor (5-10 wt. %) amounts of quartz and trace (<5 wt. %) amounts of mordenite. No trace impurities were detected in the sample from Buckhorn, New Mexico (27082). The sample from Hector, California (27022), contained minor amounts of quartz and mordenite.

For total chemical analysis samples were fused in lithium metaborate and examined by inductively coupled plasma spectroscopy. Because quartz was the only mineral other than zeolites detected by X-ray diffraction in any of the samples, all elements other than Si were assumed to have come from the zeolite. Elemental analyses of the major cations, other than Al and Si, which are part of the aluminosilicate structure, were converted from wt. % to meq/g in order to compare potential exchange capacities (Table 1).

EXPERIMENTAL PROCEDURE

Breakthrough studies were performed using 30 x 1.5-cm diameter glass columns at ambient temperatures. Each column was loosely packed with about 35 g of zeolitic tuff, yielding bed depths of about 27 cm. Actual bed depths of each column were measured and used to calculate bed volumes (BV). Columns were operated under flooded conditions using a reservoir containing 1 liter of loading solution at the top of the column.

Table 1. Possible exchangeable cations (meq/g) of clinoptilolite-rich tuffs.¹

Ionic species	Barstow, California	Buckhorn, New Mexico	Hector, California
Ca ²⁺	0.65	1.20	0.34
K ⁺	0.31	0.25	0.23
Mg ²⁺	0.34	0.91	0.16
Na ⁺	1.17	0.52	1.52
Total	2.47	2.87	2.25

¹Estimated from total chemical analysis in solution after dissolution by lithium metaborate fusion of whole rock. Inasmuch as these totals significantly exceed the cation-exchange capacities normally reported for these zeolitic tuffs, the individual values should be considered in a relative manner only.

The bottom outlet of the column was fitted with a control valve to regulate the flow rate of the effluent to 1 ml/min (≈ 1.4 BV/hr). Each column was loaded with a 0.02 N single cation solution using the sulfate salt. A 0.02 N solution of H₂SO₄ was used in the H⁺-breakthrough studies. The volume and pH of the column effluent were measured, and the effluent was analyzed for Na⁺ and for the cation studied. The effluent prior to breakthrough typically contained <1 mg/liter of the test cation and was about 0.022 N in Na⁺. 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 demonstrating cessation of ion exchange. The point at which the test cation "broke through" was considered the breakthrough point. The milliequivalents (meq) at breakthrough were determined from the accumulated volume of 0.02 N test solution at breakthrough. The effective cation-exchange capacity (meq/g) for the entering cation was then calculated based on the number of grams of zeolitic tuff in the column.

To prepare Na-exchanged material for later tests, 30 g of the clinoptilolite-rich tuff was stirred with 150 ml of 4.3 N NaCl for 4 hr. The slurry was filtered and the Na-treated material was washed with 50 ml of water to remove residual NaCl solution.

RESULTS AND DISCUSSION

Cation affinity

Data from breakthrough studies were used to determine the order of cation affinity on the three zeolitic tuffs for cations typically found in ARD. An example of a breakthrough curve for Ca²⁺ is shown in Figure 1. The data were subjected to regression analysis so that the similarities could be seen more easily. The breakthrough point for Ca²⁺ was 0.95 meq Ca²⁺/g of tuff. The shape of the Na⁺ curve is a mirror image of the Ca²⁺ curve and indicates the equivalent exchange of Na⁺ by Ca²⁺. Curves were developed for each of the test cations with each of the samples and are presented in Figures 2-8. The data were not subjected to regression analysis because some of the curves approximated step functions and could not be accurately depicted using regressed data. Sodium profiles are not included for the sake of clarity, but were all similar to that shown in Figure 1. pH is presented instead of metal concentration in normality in Figure 6 for the H⁺ breakthrough curves. The H⁺ breakthrough points were chosen to be pH 7, the pH of "pure" water.

In single cation solutions containing no competing cations, the breakthrough point is a relative measure of the affinity for that particular cation. The greater the loading prior to breakthrough, the greater the apparent affinity. Table 2 summarizes the data for the breakthrough studies that were used to predict the following orders of affinity for a 0.02 N single-cation solution:

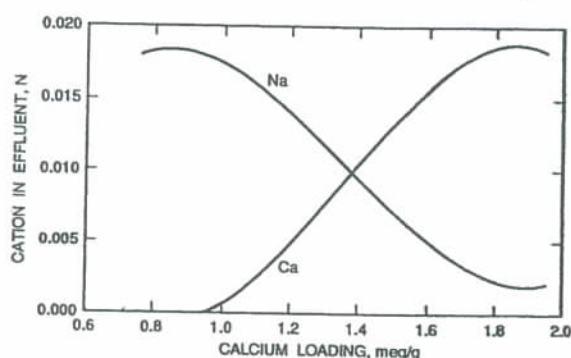


Figure 1. Effluent concentrations of Ca^{2+} and Na^{+} from a column containing clinoptilolite-rich tuff from Hector, California, after loading with 0.02 N CaSO_4 at 1.4 bed volumes/hr.

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

Buckhorn: $\text{H}^{+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+} > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Mg}^{2+}$

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

For the Barstow and Hector samples, the orders of affinity indicate that, given equinormal concentrations, Ca^{2+} is preferred over most of the other tested cations. This means that, for ARD in which the concentration of Ca^{2+} is commonly an order of magnitude greater than that of toxic cations, enough exchange capacity will be needed to remove most of the Ca^{2+} before the other cations will be able to compete successfully for exchange sites. To decrease toxic metal concentrations to the near-zero levels required for discharge, essentially all of the Ca will have to be removed.

At first glance, the Buckhorn sample would seem to be a better choice for removing Cu^{2+} and Zn^{2+} in the presence of Ca^{2+} , because Ca^{2+} is one of the last cations to exchange. The data in Table 2, however,

Table 2. Breakthrough values for three clinoptilolite-rich tuffs.

Ionic species	Barstow, California	Buckhorn, New Mexico	Hector, California
Al^{3+}	0.15	0.05	0.25
Ca^{2+}	0.65	0.10	0.95
Cu^{2+}	0.45	0.28	0.95
Fe^{2+}	0.13	0.18	0.50
H^{+}	0.28	0.30	0.36
Mg^{2+}	ND ¹	ND ¹	0.35
Zn^{2+}	0.45	0.20	1.20

¹ND = not detected

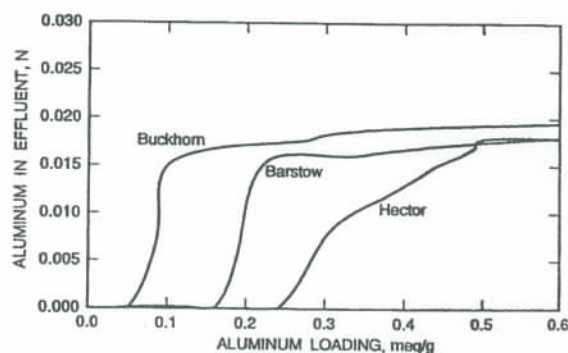


Figure 2. Al^{3+} loading on three clinoptilolite-rich tuffs after contact with 0.02 N $\text{Al}_2(\text{SO}_4)_3$ at 1.4 bed volumes/hr.

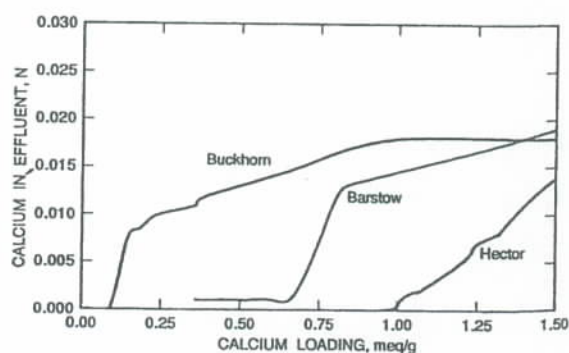


Figure 3. Ca^{2+} loading on three clinoptilolite-rich tuffs after contact with 0.02 N CaSO_4 at 1.4 bed volumes/hr.

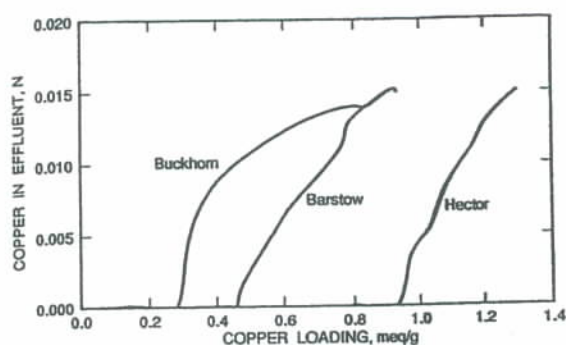


Figure 4. Cu^{2+} loading on three clinoptilolite-rich tuffs after contact with 0.02 N CuSO_4 at 1.4 bed volumes/hr.

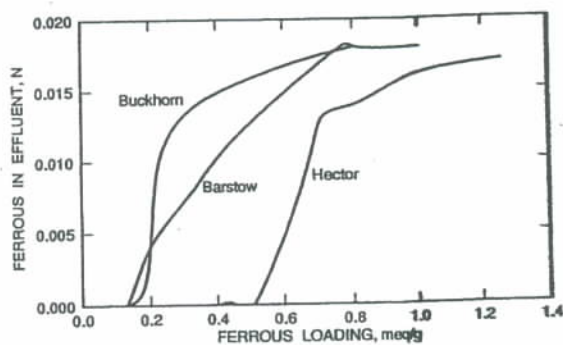


Figure 5. Fe^{2+} loading on three clinoptilolite-rich tuffs after contact with 0.02 N FeSO_4 at 1.4 bed volumes/hr.

show lower breakthrough values for Cu^{2+} and Zn^{2+} than found for the Barstow and Hector samples. The Buckhorn sample also has the highest Ca^{2+} content (Table 1), suggesting that most of the available exchange sites are already occupied by Ca^{2+} leaving little capacity for removing additional Ca^{2+} from solution. The low capacities for Cu^{2+} and Zn^{2+} indicate that these cations do not readily displace Ca^{2+} from some of the occupied exchange sites even though the affinity sequence indicates the ability to do so.

Relative order of effective cation-exchange capacity

The order of effective cation-exchange

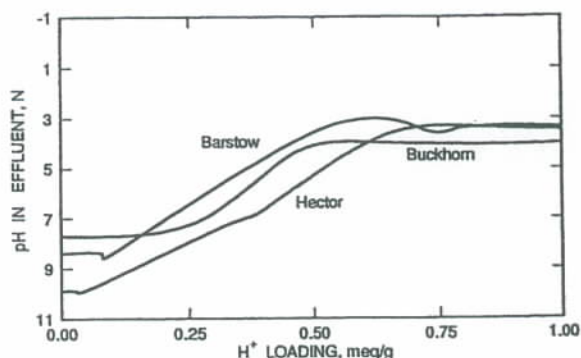


Figure 6. H^+ loading on three clinoptilolite-rich tuffs after contact with 0.02 N H_2SO_4 at 1.4 bed volumes/hr.

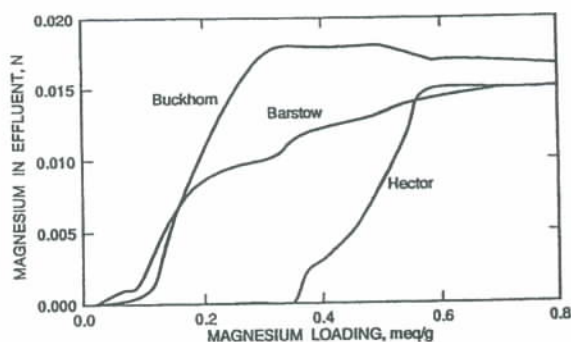


Figure 7. Mg^{2+} loading on three clinoptilolite-rich tuffs after contact with 0.02 N MgSO_4 at 1.4 bed volumes/hr.

capacity, as determined from breakthrough curves and from Table 2, is Hector > Barstow > Buckhorn. This is considered a general order because it is true for most of the cations studied: Al^{3+} , Ca^{2+} , Cu^{2+} , Mg^{2+} , and Zn^{2+} . For Fe^{2+} and H^+ the order is Hector > Buckhorn > Barstow in which the values for the Barstow and Buckhorn samples are similar and may be indistinguishable. The order Hector > Barstow > Buckhorn correlates with their relative Na^+ content (Table 1) and is consistent with Na^+ being the principal cation removed from zeolitic sites. Exchange of Na^+ was also reflected in the breakthrough studies in which

an equivalent amount of Na^+ was exchanged for each metal cation (Figure 1). Conversely, as discussed above, the presence of Ca^{2+} inhibited exchange of the other metal cations tested.

After pretreating the as-received Buckhorn sample with a NaCl solution, breakthrough increased from 0.28 meq/g for Cu^{2+} and 0.20 meq/g for Zn^{2+} (Table 2) to 1.1 and 0.80 meq/g, respectively, demonstrating that measured exchange capacities of as-received zeolitic tuffs may not accurately reflect their potential exchange capabilities for ARD.

Increase of pH of ARD water with zeolites

In all tests, the pH of the effluents prior to breakthrough were higher than that of the feed solutions. After breakthrough, the pH decreased and the metal concentrations approached that of the feed solutions. This change of pH at breakthrough for the Hector zeolitic tuff is depicted in Figures 9 and 10 for Al^{3+} and Zn^{2+} , respectively, cations having comparatively strong and weak hydrolysis constants. Because the feed solutions were prepared from reagent grade salts with no acid additions, the pH is the result of partial hydrolysis of metal cations according to the following reaction:



Hydrolysis of metal cations (M^{z+}) drives the above equation to the right and lowers the pH. Conversely, the removal of cations reverses the equation and pH increases.

Further evidence for hydrolysis can be found by comparing the pH after breakthrough in Figures 9 and 10. The pH of the Al^{3+} solution decreased to about 4, lower than the pH of about 6 for the Zn^{2+} solution. The hydrolysis constants for Al^{3+} and Zn^{2+} , respectively, are 2.51×10^{-5} and 5.89×10^{-10} (Sillen and Martel, 1964), meaning that Al^{3+} hydrolyzes more strongly than Zn^{2+} and its

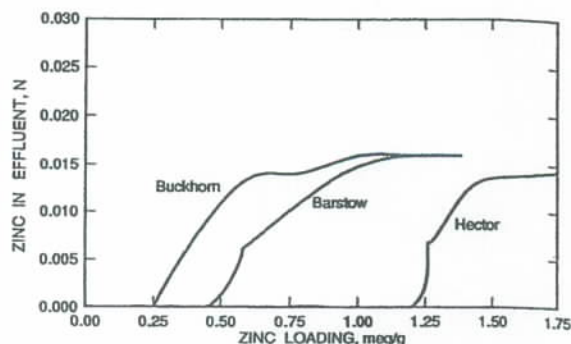


Figure 8. Zn^{2+} loading on three clinoptilolite-rich tuffs after contact with 0.02 N ZnSO_4 at 1.4 bed volumes/hr.

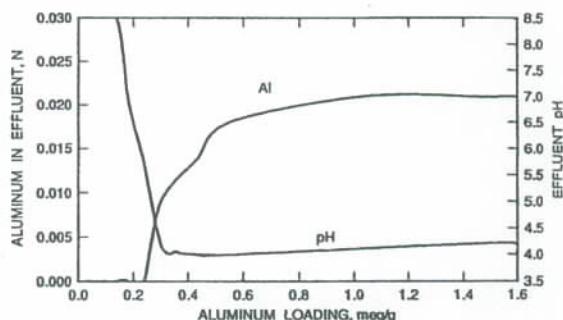


Figure 9. Al^{3+} concentration and pH of effluent from a column containing clinoptilolite-rich tuff from Hector, California, after loading with 0.02 N $\text{Al}_2(\text{SO}_4)_3$ at 1.4 bed volumes/hr.

solution pH should be lower. Considering the above evidence and the fact that mass balances (Figure 1) demonstrate a one-for-one exchange of Na^+ for the test cations, the change in pH was probably principally due to changes in hydrolysis equilibria and not to the co-uptake of H^+ with the metal cations.

SUMMARY AND CONCLUSIONS

The results of this study have demonstrated that the clinoptilolite-rich tuffs ex-

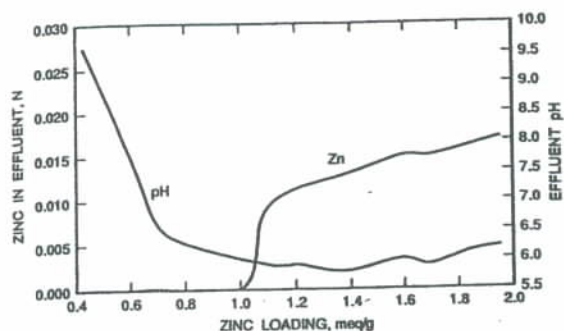


Figure 10. Zn^{2+} concentration and pH of effluent from a column containing clinoptilolite-rich tuff from Hector, California, after loading with 0.02 N $ZnSO_4$ at 1.4 bed volumes/hr.

changed Na^+ for seven cations commonly found in ARD. Increased pH of treated solutions was a result of shifts in the equilibrium of the hydrolysis reactions, rather than of the uptake of H^+ by the zeolites.

Loading characteristics for the cations were measured for three samples of clinoptilolite-rich tuff using single-cation sulfate solutions at 0.02 N. Plots of loading capacities were used to determine the following cation affinities:

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

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

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

The general order of effective cation-exchange (i.e., loading) capacity at breakthrough for the three test samples was: Hector > Barstow > Buckhorn and corresponds to the Na^+ content of the zeolite. The

order of both cation affinities and effective exchange capacities were influenced by the Ca^{2+} content of the sample. The cation-exchange capacity of an as-received zeolitic tuff containing a high Ca to Na ratio was enhanced by pretreatment with a NaCl solution to exchange Ca^{2+} for Na^+ .

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