

## SODIUM, CALCIUM, AND AMMONIUM EXCHANGE ON CLINOPTILOLITE FROM THE FORT LACLEDE DEPOSIT, SWEETWATER COUNTY, WYOMING

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**Abstract**—Clinoptilolite from the Fort LaCledé deposit in Sweetwater County, Wyoming, shows a moderate selectivity for  $\text{NH}_4^+$  over  $\text{Na}^+$  in aqueous solution. At  $30^\circ\text{C}$ , the standard free energy of this replacement reaction is  $-0.7$  kcal/mole at an ionic strength of  $0.05$  M and  $-0.8$  kcal/mole at  $0.5$  M. The  $\text{Na}^+$ - $\text{NH}_4^+$  exchange is complete within 3 days in agitated solution and proceeds to the same extent from the clinoptilolite saturated with either cation.

The  $\text{Ca}^{2+}$ - $\text{Na}^+$  exchange also is complete within 3 days in agitated aqueous solution and proceeds to the same extent from either the calcium or the sodium form of the zeolite. Using test methods which take into account the slower equilibration of  $\text{Ca}^{2+}$ -loaded clinoptilolite, the cation-exchange capacity is substantially the same over the full range of loading by  $\text{Ca}^{2+}$  and  $\text{Na}^+$ .  $\text{Ca}^{2+}$  replaces  $\text{Na}^+$  with decreasing selectivity as  $\text{Ca}^{2+}$  loading increases to about 80% at  $30^\circ\text{C}$  (95% at  $63^\circ\text{C}$ ), above which the selectivity reverses. The standard free energy of replacement of two  $\text{Na}^+$  ions by one  $\text{Ca}^{2+}$  ion in  $0.05$  M solution is  $-1.2 \pm 0.2$  kcal/mole at  $63^\circ\text{C}$  and  $-0.3$  to  $-0.8$  kcal/mole at  $30^\circ\text{C}$ .

**Key Words**—Ammonium, Calcium, Cation exchange, Clinoptilolite, Selectivity, Sodium.

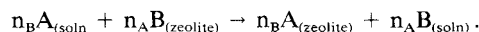
### INTRODUCTION

The value of natural zeolites in many applications is largely dependent upon their cation-exchange characteristics (Mumpton, 1978; Dyer, 1984). Such applications include purification of water and wastewater, sequestering radionuclides, improvement of agricultural soils, and supplementation of animal feeds. Of particular interest in agricultural and water-treatment applications is the exchange of the cation resident on the zeolite with  $\text{NH}_4^+$  or  $\text{Ca}^{2+}$  (McNair *et al.*, 1986). Ames (1960, 1961) investigated the exchange competition of various cations with  $\text{Cs}^+$  on clinoptilolite and reported separate selectivity series for monovalent and divalent cations. He reported that the selectivity for  $\text{NH}_4^+$  is greater than that for  $\text{Na}^+$ . Ames' work was cited by Vaughan (1978) who specified the selectivity relationship  $\text{Na}^+ > \text{Ca}^{2+}$  and by Semmens and Seyfarth (1978) who specified the selectivity relationship  $\text{Ca}^{2+} > \text{Na}^+$ . The investigations of cation exchange properties of clinoptilolite reported here were undertaken to clarify the  $\text{Ca}^{2+}$ - $\text{Na}^+$  selectivity and to enhance the scientific basis for commercial development of agronomic and water-purification applications.

### THERMODYNAMIC PARAMETERS

The equilibrium constants and the free energy of an exchange reaction on a solid ion exchanger have been described by Gaines and Thomas (1953). For the re-

placement of ion B of charge  $n_B$  by ion A of charge  $n_A$ , the exchange reaction is



Conventionally, the equivalent fraction of evictor ion A in the solution,  $A_s$ , and on the zeolite,  $A_z$ , is defined as the number of equivalents of ion A in the particular phase divided by the sum of the equivalents of both ions in that phase. The mass action expression,  $K_s$ , for the exchange reaction written above can be expressed as

$$K_s = \frac{(A_z)^{n_B}(1 - A_z)^{n_A}}{(A_s)^{n_B}(1 - A_s)^{n_A}} \quad (1)$$

At a given temperature and solution composition,  $K_s$  (which is sometimes termed the selectivity coefficient) expresses the relative preference of the zeolite for evictor ion A over resident ion B. Correction for the activities of the ions in solution results in the corrected selectivity coefficient,  $K_c$ :

$$K_c = \frac{K_s(f_B)^{n_A}}{(f_A)^{n_B}} \quad (2)$$

where  $f_A$  and  $f_B$  are activity coefficients in the solution for evictor and resident ions, respectively. The natural logarithm of the thermodynamic equilibrium constant for the exchange reaction can be expressed in terms of  $K_c$  by:

$$\ln K = (n_B - n_A) + \int_0^1 (\ln K_c) dA_z - n_A n_B \left[ \int_1^{a_w(A)} q_w(A) d(\ln a_w) - \int_1^{a_w(B)} q_w(B) d(\ln a_w) + \int_{a_w(A)}^{a_w(B)} q_w(A, B) d(\ln a_w) \right], \quad (3)$$

where  $a_w$  represents the activity of water in the various limiting solutions and  $q_w$  represents the content of water in the zeolite in the indicated cationic forms (Barrer *et al.*, 1966). The terms in Eq. (3) involving the activity and content of water are customarily neglected in thermodynamic treatments of zeolites (Breck, 1974) and have been demonstrated to be negligible for synthetic zeolite A (Barrer *et al.*, 1963). The resultant form of Eq. (3),

$$\ln K = (n_B - n_A) + \int_0^1 (\ln K_c) dA_z, \quad (4)$$

allows calculation of the thermodynamic equilibrium constant without knowledge of the ratio of the activity coefficients for the cations on the clinoptilolite.

A plot of the logarithm of  $K_c$  vs.  $A_z$ , termed a Kieland plot, can be used to evaluate the integral of Eq. (4). Such curves may have many forms, but for univalent exchange ( $n_A = n_B = 1$ ), the plots generally are linear (Breck, 1974).

## EXPERIMENTAL

### Zeolite characterization

The material investigated was collected from an outcrop of blue-green tuff in the Fort LaClède deposit, Sweetwater County, Wyoming. Some characteristics of this deposit have been described by Curry and Santini (1983). Roehler (1973) described the robin's-egg-blue marker bed (tuff) from which the material was collected as part of the Adobe Town Member of the Eocene Washakie Formation. A 20 × 50 mesh working sample was prepared by crushing and screening and was then subsampled for experimental work. Clinoptilolite was identified as the predominant mineral phase by X-ray powder diffraction (XRD); quartz was detected in trace amounts, but no other mineral phases were recognized by XRD. The cation-exchange capacity (CEC) of the <200-mesh samples is 1.8 meq/g, as determined by the American Society of Agronomy method (Black, 1965); the extractable cations are  $\text{Na}^+$  (1.3 meq/g),  $\text{Ca}^{2+}$  (0.5 meq/g), and  $\text{K}^+$  (0.2 meq/g). Scanning electron microscopy (Figures 1 and 2) showed the sample to consist of clinoptilolite crystals typically smaller than 10  $\mu\text{m}$  in diameter, grading into sub-micrometer size grains. Euhedral morphology was observed in the finer

grains to the limit at which they became electron translucent.

### Cation-exchange experiments

Portions of the working sample of clinoptilolite were converted to the ammonium, calcium, and sodium forms by contact with concentrated aqueous solutions of the appropriate chlorides followed by washing with deionized water until the wash water gave no precipitate with  $\text{AgNO}_3$ . Exchange and washing were facilitated by use of a 1-liter Imhoff cone which had been modified by the addition of tubing connections at the bottom and near the top. Solutions were passed upward through zeolite (about 200 g) in the cone at a controlled rate sufficient to fluidize the zeolite. Each salt solution was divided into portions which contained at least five times the cation required to saturate the zeolite. The zeolite in the cone was allowed to drain before each fresh portion of the solution was added, and the solution was recirculated intermittently so that the zeolite was fluidized for a minimum of 20 min with each portion.

Determinations of the  $\text{Na}^+\text{-NH}_4^+$  and the  $\text{Na}^+\text{-Ca}^{2+}$  exchange competitions were carried out in covered 1-liter Erlenmeyer flasks, each containing 500 ml of exchange solution and 0.5 g of the dried clinoptilolite. All experiments were performed in duplicate. For each competition, a series of solutions containing varying ratios of the pair of cations was prepared using the reagent-grade nitrates and deionized water. Portions of each solution of the two series were agitated separately with samples of the fully exchanged cationic forms of the zeolite in a thermostated shaking water bath for 3 days. To check for possible hysteresis, two complete series of experiments were performed for each competition, one with each limiting cationic form of the zeolite. Only minor production of fines was observed at the end of the agitation, possibly because the Fort LaClède clinoptilolite is relatively abrasion resistant or because weak particles disaggregate and are flushed away during preparation of the fully exchanged zeolite in the fluidized bed.

Loadings of the various cations on the zeolite were determined by contacting the zeolite with 1 M aqueous  $\text{CsCl}$ , filtering the solution through a 5- $\mu\text{m}$  perfluorocarbon filter (Millipore type LS), diluting to volume, and measuring ammonia nitrogen in the solution by the micro-Kjeldahl method and other cations by atomic absorption spectroscopy. For the ammonium and sodium forms of the zeolite, three 5-min contacts each with 5 ml of the  $\text{CsCl}$  solution were sufficient to recover the cations; however, as more calcium was exchanged into the zeolite, longer contact with the  $\text{CsCl}$  was required to recover the cations. For example, clinoptilolite samples having a ratio of exchangeable  $\text{Ca}:\text{Na}$  in excess of 10:1 showed that only about half of the cations were recovered with three 5-min contacts with 5

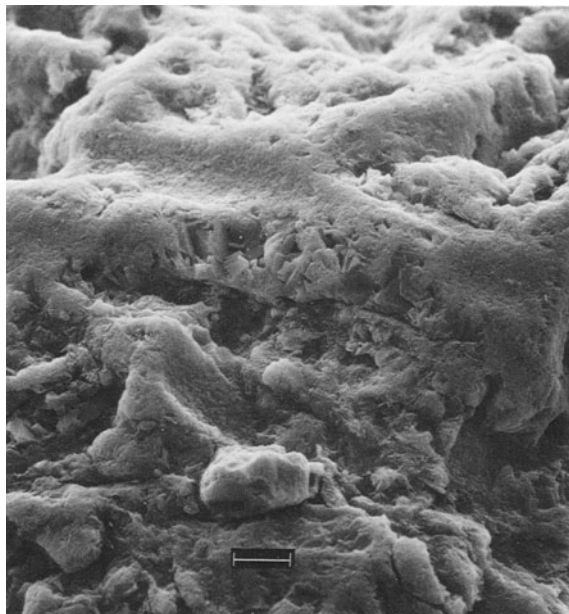


Figure 1. Scanning electron photomicrograph of Fort LaCledde clinoptilolite showing typical pseudomorphic structure of particle surfaces. Scale bar indicates 10  $\mu\text{m}$ .

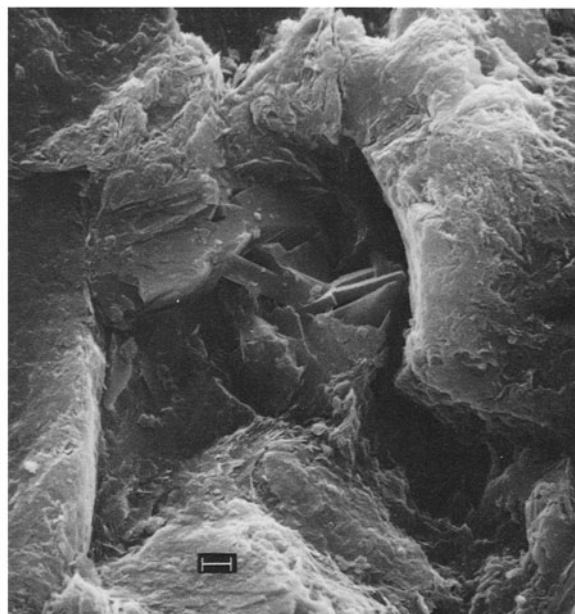


Figure 2. Scanning electron photomicrograph of Fort LaCledde clinoptilolite showing relatively large crystals grading into sub-micrometer-size grains. Scale bar indicates 1  $\mu\text{m}$ .

ml of the CsCl. When corrections were made for this failure of the initial experimental procedure, the CEC of the zeolite remained nearly constant over the full range of exchange conditions studied. The aluminum content of the final solutions was measured to make certain that the clinoptilolite had been removed in the filtration step. Results were discarded if the aluminum content was more than about twice the analytical detection limit (about 0.1 ppm in the absence of  $\text{Ca}^{2+}$  and 1 ppm in its presence).

## RESULTS AND DISCUSSION

### *Sodium-ammonium ion competition*

The competition between  $\text{NH}_4^+$  and  $\text{Na}^+$  for exchange sites on Fort LaCledde clinoptilolite was followed at 30°C and at ionic strengths of 0.05 and 0.5 M. Figure 3 shows a plot of the ion fraction of  $\text{NH}_4^+$  on the zeolite vs. the ion fraction in solution. With the exception of two points for the  $\text{NH}_4^+$ -zeolite at high ionic strength, the plots show no hysteresis, and no significant difference between the two ionic strengths is apparent.

The activity coefficient of  $\text{Na}^+$  in the dilute solutions is 2% more than that of  $\text{NH}_4^+$  according to the estimates of single ion activities obtained from Kielland's technique using the extended Debye-Huckel treatment (Laitinen, 1960). By the same technique, the activity coefficient of  $\text{Na}^+$  in the solutions of 0.5 M ionic strength is 10% greater than that of  $\text{NH}_4^+$ . Applying these activity corrections to the data of Figure 3 results in the Kielland plot shown in Figure 4. This plot shows

the corrected selectivity coefficient for  $\text{NH}_4^+$  replacing  $\text{Na}^+$ . The lines fitted to the two data sets display negative slopes with increasing  $\text{NH}_4^+$  on the zeolite. The negative slope indicates that  $\text{NH}_4^+$  is less strongly preferred over  $\text{Na}^+$  by the zeolite as the zeolite is progressively converted to the ammonium form.

From the Kielland plots of Figure 4, the thermodynamic equilibrium constants for the conversion of the sodium zeolite to the ammonium form can be determined. At an ionic strength of 0.05 M, the equilibrium constant is  $3.3 \pm 0.2$ ; at an ionic strength of 0.5 M, it is  $3.8 \pm 0.4$ . The corresponding standard free energies for the reaction are  $-0.7$  kcal/mole at the lower ionic strength and  $-0.8$  kcal/mole at the higher. These values are somewhat smaller than that determined at 0.02 M for the Hector clinoptilolite by Howery and Thomas (1965) ( $-1.3$  kcal/mole at 30°C) and by Barrer *et al.* (1967) ( $-1.3$  kcal/mole recalculated from their determination at 60°C to the 30°C value by use of the enthalpy value reported by Howery and Thomas (1965)).

### *Sodium-calcium ion competition*

The  $\text{Na}^+$ - $\text{Ca}^{2+}$  competition experiments were carried out at a total molarity of 0.05 M and at 30° and 63°C. The higher temperature was employed because one possible explanation of earlier conflicting results is that the entry of the large hydrated calcium ion into the zeolite structure may require significant activation energy. Results of these experiments are summarized in Figure 5. This illustration shows that there is no marked

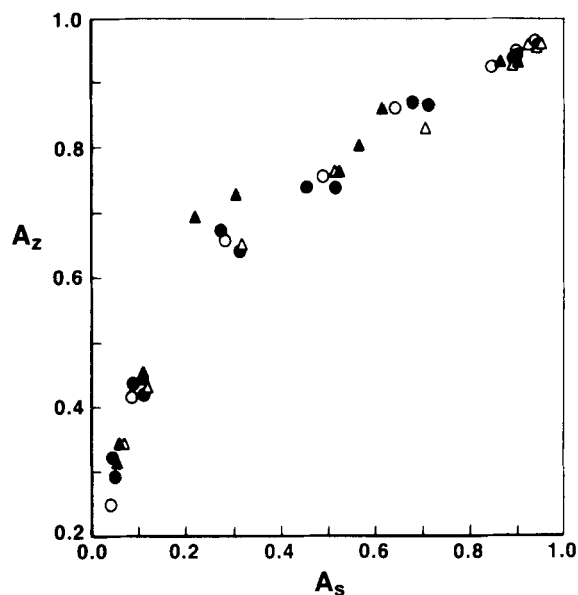


Figure 3. Plot of ion fraction of  $\text{NH}_4^+$  on Fort LaCledde clinoptilolite ( $A_z$ ) vs. ion fraction in solution ( $A_s$ ) for competition between  $\text{Na}^+$  and  $\text{NH}_4^+$  at  $30^\circ\text{C}$ . Circles = exchange beginning with the sodium form; triangles = exchange beginning with the ammonium form. Open symbols = solutions of 0.05 M ionic strength; solid symbols = 0.5 M ionic strength.

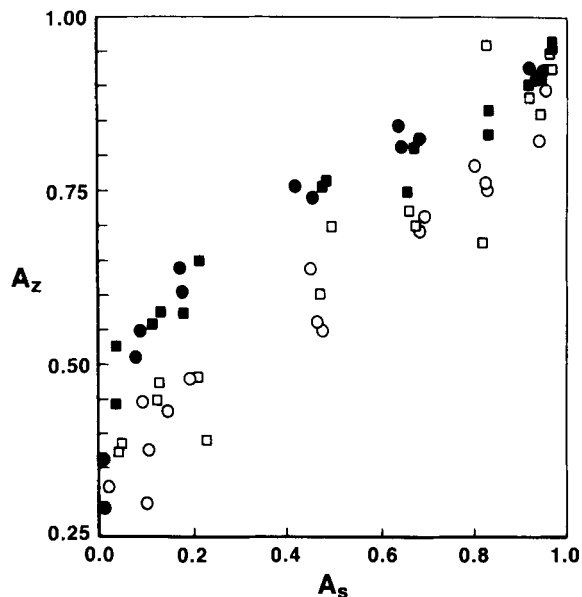


Figure 5. Plot of the ion fraction of calcium on Fort LaCledde clinoptilolite ( $A_z$ ) vs. ion fraction in solution ( $A_s$ ) for competition between  $\text{Na}^+$  and  $\text{Ca}^{2+}$  at 0.05 M. Circles = exchange beginning with the sodium form; squares = exchange beginning with the calcium form. Open symbols = exchange at  $30^\circ\text{C}$ ; solid symbols = exchange at  $63^\circ\text{C}$ .

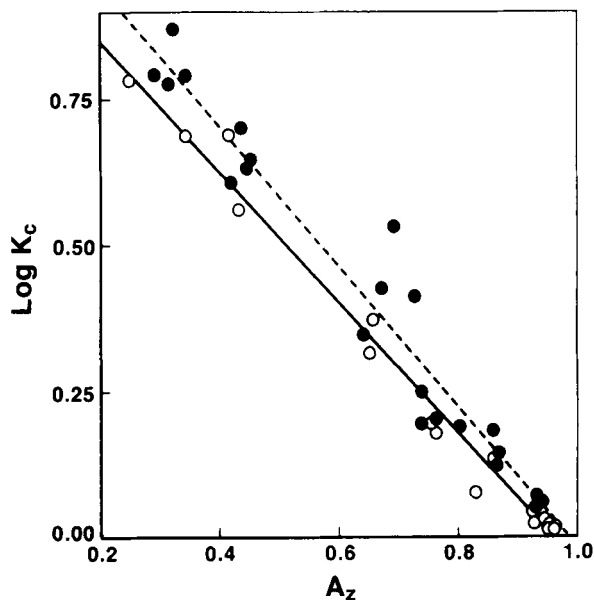


Figure 4. Kielland plot of corrected selectivity coefficient ( $K_c$ ) vs. ion fraction on the zeolite ( $A_z$ ) for  $\text{NH}_4^+$  replacing  $\text{Na}^+$  on Fort LaCledde clinoptilolite at  $30^\circ\text{C}$ . Open symbols and solid line fit by linear least squares are for solutions of 0.05 M ionic strength; solid symbols and dashed line are for 0.5 M ionic strength.

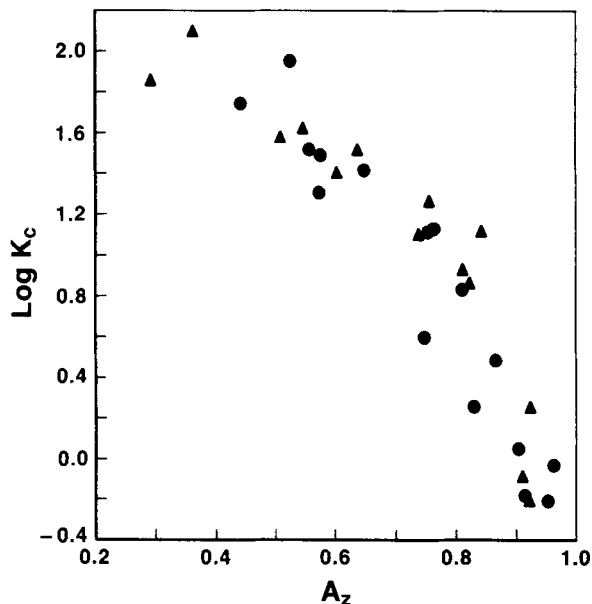


Figure 6. Kielland plot of corrected selectivity coefficient ( $K_c$ ) vs. ion fraction on the zeolite ( $A_z$ ) for  $\text{Ca}^{2+}$  replacing  $\text{Na}^+$  on Fort LaCledde clinoptilolite at  $63^\circ\text{C}$ . Circles = exchange beginning with the sodium form; triangles = exchange beginning with the calcium form.

hysteresis in the exchange under the test conditions, that the zeolite preferentially takes up  $\text{Ca}^{2+}$  over  $\text{Na}^+$  at low to moderate loadings of  $\text{Ca}^{2+}$ , and that the preference for  $\text{Ca}^{2+}$  is somewhat greater at the higher temperature. To put these observations into a quantitative form, the equilibrium constants were determined using the Kielland plots, such as that shown in Figure 6, and following the procedure outlined by Wiers *et al.* (1982).

The thermodynamic equilibrium constants for the replacement of two  $\text{Na}^+$  by one  $\text{Ca}^{2+}$  on the Fort LaCledé clinoptilolite are 6 at 63°C and 2 at 30°C. As noted above, shapes of the Kielland plot curves are unknown; therefore, to perform the required integration, simple curves were chosen to represent the experimental data. Uncertainties in this approximation resulted in a range for  $K$  of 4.5 to 7.9 at 63°C and of 1.8 to 3.8 at 30°C. The corresponding values of  $\Delta G^\circ$  are  $-1.2$  kcal/mole ( $\pm 0.2$  kcal/mole) at 63°C and  $-0.4$  kcal/mole ( $-0.4$  to  $+0.1$  kcal/mole) at 30°C.

These results indicate that the Fort LaCledé clinoptilolite at 30°C has a moderate selectivity for  $\text{Ca}^{2+}$  over  $\text{Na}^+$  at  $<80\%$   $\text{Ca}^{2+}$  loading. Above this loading, the zeolite is slightly selective for  $\text{Na}^+$ . At 63°C, the zeolite has somewhat greater affinity for  $\text{Ca}^{2+}$  at all loadings than it does at 30°C. The  $\text{Na}^+$ - $\text{Ca}^{2+}$  exchange proceeding in either direction in agitated solution is complete or nearly complete within 3 days. The CEC of the clinoptilolite remains at about 1.8 meq/g over the full range of loadings with  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , provided that the procedure for determining CEC allows for the fact that calcium-loaded zeolite may be relatively slow (scale of minutes) to exchange with the displacing ion.

Selectivity for  $\text{Ca}^{2+}$  suggests possible application of the Fort LaCledé clinoptilolite as a builder for laundry detergent (Llenado, 1984). Synthetic zeolite A, however, shows higher selectivity (Rees, 1984) and is produced as a finely divided, white powder. The projected costs for producing material of particle size appropriate for detergents suggest that the clinoptilolite from the Fort LaCledé deposit is not an attractive alternative for this application. Utilization of the exchange properties of the clinoptilolite in agronomic (sequestering calcium in soil) or animal-feeding applications, on the other hand, are more promising. In these applications, particle sizes greater than 100 mesh are generally desirable, color is unimportant, and the exchange kinetics of the clinoptilolite are appropriate for the time scales of hours to months.

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