Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Tsuji, Masamichi and Komarneni, Sridhar(1993) 'Selectivity Study of Alkaline Earth and Divalent Transition Metal Ions on [Al^3 Na]-Substituted Tobermorites', Separation Science and Technology, 28: 11, 2061 — 2071
To link to this Article: DOI: 10.1080/01496399308016734
URL: http://dx.doi.org/10.1080/01496399308016734

SEPARATION SCIENCE AND TECHNOLOGY, **28**(11&12), pp. 2061–2071, 1993

Selectivity Study of Alkaline Earth and Divalent Transition Metal Ions on [Al^{3+} + Na^+]-Substituted Tobermorites

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ABSTRACT

The ion-exchange selectivities of [Al^{3+} + Na^+]-substituted tobermorites with 1–20 mol% substitution of aluminum for silicon at low loadings were investigated for Mg^{2+}, Sr^{2+}, Ba^{2+}, and Ni^{2+}. The selectivity order depended on the degree of substitution, exchanging medium, and loading of metal ions, reflecting different types of ion-exchange sites in the Al^{3+}-substituted tobermorites which are an interesting group of calcium aluminosilicate cation exchangers.

INTRODUCTION

Tobermorite, $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$, is a naturally occurring hydrous calcium silicate and can be synthesized under hydrothermal conditions using reactive CaO and SiO_2 compounds. Isomorphous substitution of Al^{3+} for Si^{4+} in the dreierketten (chains) of tobermorite creates a negative charge which is compensated for by alkali and alkaline earth cations. The alkali and alkaline earth cations are loosely bound and are responsible for cation exchange (1, 2). The 1.13-nm tobermorite substituted by [Al^{3+} + Na^+] for Si^{4+} showed especially high selectivity for Cs^+ (1). The exchange cavity is located between the CaO layer linked to $Si_3(O/OH)_9$ (2). At least three different cation-exchange sites may exist in substituted tobermorites: site A, alkali cation coming from substitution of Al for Si; site B, loosely bound Ca within the above cavity; and site C, Ca site in the CaO layer (2). Unsubstituted calcium silicates such as xonotlite, tobermor-

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ite, and wollastonite have been found to exhibit some specific and irreversible cation-exchange properties with Ca in site C for divalent transition metal ions (3–6). The objective of this research was to identify the available ion-exchange sites in Al^{3+}-substituted tobermorites through a selectivity study of several divalent metal ions.

EXPERIMENTAL PROCEDURE

Preparation of Tobermorites with Different Levels of Al^{3+} Substitution

The synthesis procedure (7) is as follows: silica gel ($SiO_2 \cdot 0.26H_2O$), CaO, and $NaAlO_2$ were mixed in a Teflon vessel in the desired mole ratios. Sixty milliliters of deionized water was added with stirring and the mixture was heated at 175°C for 4 days in a Parr bomb. The aggregated product was broken in the vessel after cooling and washed three times with deionized water to remove soluble components by a centrifuge. Then it was dried at 60°C until a constant weight was obtained; this took about 2 days. The supernatant solution and the washings were collected for chemical analysis of Al^{3+}, Ca^{2+}, Na^{+}, and Si^{4+}. The products were identified by powder x-ray diffraction (XRD) using a Philips x-ray diffractometer with Ni-filtered CuK_α radiation. The chemical composition was determined from the difference between the initial amounts and the remaining amounts in the above solution collected for chemical analysis. The water content of the tobermorite was determined from the weight loss after heating at 900°C. In addition to these substituted tobermorites, a synthetic xonotlite was used in some experiments and its preparation was reported elsewhere (4).

Distribution Coefficients (K_d)

A 0.0250-g portion of the as-prepared tobermorite or xonotlite, or the Ca^{2+} form of tobermorite, was equilibrated with 25 mL of different concentrations of NaCl, $CaCl_2$, NH_4Cl, or $Ca(OOCH_3)_2$ solution containing 10^{-4} N metal chloride at 25°C. After equilibration for 2 weeks, the solid and solution phases were separated, and the supernatant solution was analyzed for metal ions by atomic emission spectrometry (AES) using a Spectra-Metrics Spectra-Span III instrument or atomic absorption spectrophotometry (AAS) using a Perkin-Elmer PE 703 instrument with an electrode-less discharge lamp. The amounts of metal ions exchanged by the exchanger were determined from the difference in the concentration between the sample and the reference. The K_d was calculated by the following equation with an estimated error of ±2%:

$$K_d = \frac{\text{amount of metal ions exchanged (meq/g)}}{\text{equilibrium concentration of metal ions (meq/mL)}} \tag{1}$$

THEORETICAL BASIS

Formulation of K_d Based on the Thermodynamic Consideration

The cation-exchange reactions between Na^+ and M^{n+} are represented by

$$n\overline{\mathrm{Na}}^+ + \mathrm{M}^{n+} \leftrightarrow \overline{\mathrm{M}}^{n+} + n\mathrm{Na}^+ \tag{2}$$

The thermodynamic equilibrium constant, K, is defined by

$$K = \frac{\overline{\mathrm{X}}_{\mathrm{M}}[\mathrm{Na}^+]^n f_{\mathrm{M}} \gamma_{\mathrm{Na}}^n}{\overline{\mathrm{X}}_{\mathrm{Na}}^n [\mathrm{M}^{n+}] f_{\mathrm{Na}}^n \gamma_{\mathrm{M}}} \tag{3}$$

In these equations the bar on a character denotes the exchanger phase, $\overline{\mathrm{X}}_{\mathrm{M}}$ and $\overline{\mathrm{X}}_{\mathrm{Na}}$ are equivalent ion fractions in the exchanger, and f_{M} and f_{Na} are the activity coefficients for the ion in the exchanger. $[\mathrm{M}^{n+}]$ and $[\mathrm{Na}^+]$ are molalities of the above two exchanging ions in solution, where they have activity coefficients γ_{M} and γ_{Na} which are unity when $[\mathrm{M}^{n+}]$ and $[\mathrm{Na}^+]$ approach zero. The standard states chosen are such that f_{M} and f_{Na} are unity when the exchanger is in its pure M^{n+} and pure Na^+ form, respectively.

Molalities $[\mathrm{M}^{n+}]$ and $[\mathrm{Na}^+]$ are replaced by the equivalent ion fractions:

$$\mathrm{X}_{\mathrm{M}} = \frac{n[\mathrm{M}^{n+}]}{n[\mathrm{M}^{n+}] + [\mathrm{Na}^+]}, \qquad \mathrm{X}_{\mathrm{Na}} = \frac{[\mathrm{Na}^+]}{n[\mathrm{M}^{n+}] + [\mathrm{Na}^+]} \tag{4}$$

$$\overline{\mathrm{X}}_{\mathrm{M}} = \frac{n[\overline{\mathrm{M}}^{n+}]}{n[\overline{\mathrm{M}}^{n+}] + [\overline{\mathrm{Na}}^+]}, \qquad \overline{\mathrm{X}}_{\mathrm{Na}} = \frac{[\overline{\mathrm{Na}}^+]}{n[\overline{\mathrm{M}}^{n+}] + [\overline{\mathrm{Na}}^+]} \tag{5}$$

and

$$\mathrm{X}_{\mathrm{M}} + \mathrm{X}_{\mathrm{Na}} = 1, \qquad \overline{\mathrm{X}}_{\mathrm{M}} + \overline{\mathrm{X}}_{\mathrm{Na}} = 1 \tag{6}$$

By using the total normality (TN) and the total capacity (TC), which are kept constant in the ion-exchange process,

$$n[\mathrm{M}^{n+}] + [\mathrm{Na}^+] = \mathrm{TN} \quad \text{and} \quad n[\overline{\mathrm{M}}^{n+}] + [\overline{\mathrm{Na}}^+] = \mathrm{TC} \tag{7}$$

Then Eq. (3) becomes

$$K = \frac{\overline{\mathrm{X}}_{\mathrm{M}} \mathrm{X}_{\mathrm{Na}}^n}{\overline{\mathrm{X}}_{\mathrm{Na}}^n \mathrm{X}_{\mathrm{M}}} \eta \Gamma \tag{8}$$

where

$$\eta = n(\mathrm{TN})^{n-1}, \qquad \Gamma = \frac{\gamma_{\mathrm{Na}}^{n} f_{\mathrm{M}}}{\gamma_{\mathrm{M}} f_{\mathrm{Na}}^{n}} \tag{9}$$

Application of the Gibbs–Duhem equation to the ion-exchange system gives for K:

$$\ln K = (1 - n) + \int_{0}^{1} \ln K_{\mathrm{Na}}^{\mathrm{M}}\, d\overline{\mathrm{X}}_{\mathrm{M}} + \Delta \tag{10}$$

where $K_{\mathrm{Na}}^{\mathrm{M}}$, the selectivity coefficient, is defined as

$$K_{\mathrm{Na}}^{\mathrm{M}} = \frac{\overline{\mathrm{X}}_{\mathrm{M}} \mathrm{X}_{\mathrm{Na}}^{n} \gamma_{\mathrm{Na}}^{n}}{\overline{\mathrm{X}}_{\mathrm{Na}}^{n} \mathrm{X}_{\mathrm{M}} \gamma_{\mathrm{M}}} \eta \tag{11}$$

The third term on the right, Δ, of Eq. (10) is negligible when compared with the experimental accuracy in measuring the equilibrium (8, 9). A plot of log $K_{\mathrm{Na}}^{\mathrm{M}}$ vs $\overline{\mathrm{X}}_{\mathrm{M}}$ (Kielland plot) often produces a straight line with a slope of $2C$ for a single-site ion exchanger and then can be expressed by

$$\log K_{\mathrm{Na}}^{\mathrm{M}} = 2C\overline{\mathrm{X}}_{\mathrm{M}} + \log(K_{\mathrm{Na}}^{\mathrm{M}})_{\mathrm{X}_{\mathrm{M}},\overline{\mathrm{X}}_{\mathrm{M}} \to 0} \tag{12}$$

where C refers to the Kielland coefficient.

The expression of the K_d value at infinitesimal loading can be derived from the Kielland plot as follows. Equations (6) and (11) are combined to give

$$K_{\mathrm{Na}}^{\mathrm{M}} = \frac{\overline{\mathrm{X}}_{\mathrm{M}}(1 - \mathrm{X}_{\mathrm{M}})^{n} \gamma_{\mathrm{Na}}^{n}}{(1 - \overline{\mathrm{X}}_{\mathrm{M}})^{n} \mathrm{X}_{\mathrm{M}} \gamma_{\mathrm{M}}} \eta \tag{13}$$

K_{d}^{M} values at any loading are given by

$$K_{d}^{\mathrm{M}} = \frac{(\mathrm{TC})\overline{\mathrm{X}}_{\mathrm{M}}}{(\mathrm{TN})\mathrm{X}_{\mathrm{M}}} \tag{14}$$

Therefore, as derived previously from the above equations (10),

$$\log(K_{d}^{\mathrm{M}})_{\mathrm{X}_{\mathrm{M}},\mathrm{X}_{\mathrm{M}} \to 0} = \log \frac{\mathrm{TC}}{n} + \log(K_{\mathrm{Na}}^{\mathrm{M}})_{\mathrm{X}_{\mathrm{M}},\mathrm{X}_{\mathrm{M}} \to 0} + \log \frac{\gamma_{\mathrm{M}}}{\gamma_{\mathrm{Na}}^{n}} - n \log(\mathrm{TN}) \tag{15}$$

The ratio of the activity coefficient will not change very drastically even though TN decreases tenfold when neutral salt media are used (8). Hence, all of the terms except for the last one on the right-hand side of Eq. (15) may be regarded as a constant. Thus, Eq. (15) states that the slope of plot of $\log(K_{d}^{\mathrm{M}})_{\mathrm{X}_{\mathrm{M}},\overline{\mathrm{X}}_{\mathrm{M}} \to 0}$ vs log(TN) is $-n$. This was well demonstrated for K_d measurements on Al^{3+}-substituted tobermorite (10).

RESULTS AND DISCUSSION

Chemical Composition of Tobermorites

Al^{3+}-substituted tobermorite compositions were formulated in the form of a tobermorite composition, $Ca_5Na_xAl_ySi_zO_{16}(OH)_2 \cdot nH_2O$ (Table 1). All the products contain H_2O in excess of the proposed formula of tobermorite, $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$. The excess water may be related to the crystallization water. In the tobermorite structure, Al^{3+} ions substitute for the tetrahedral Si^{4+} ions, which results in a negative charge in the layers. The charges are thought to be neutralized by Na^+ and/or Ca^{2+} ions in the interlayer cavity formed by the $\equiv Si—O—Si \equiv$ bridge, the CaO layer, and the $Si_3(O/OH)_9$ chain. Thus, the calculated capacity was estimated based on the Al^{3+}-contents (Table 1). Al^{3+} ions were confirmed to substitute for Si^{4+} ions in the tobermorite structure by ^{27}Al and ^{29}Si MASNMR studies (7).

Selectivity for Alkaline Earth Metal Ions in $CaCl_2$ Solution

A high selectivity for Ba^{2+} was found in all substituted tobermorites studied: $Ba^{2+} > Sr^{2+}$, Mg^{2+} (Fig. 1). The selectivity for Ba^{2+} increased with increasing Al-substitution in tobermorite. This may be because of the steric limitation of the rigid ion-exchange cavity between 2:1 layers of Al^{3+}-substituted tobermorite which limits the exchange to less hydrated cations. The deficient charge from the substitution is originated in the cavity and is neutralized by Na^+ cations which are exchangeable. In tobermorites with low Al^{3+} substitutions, the slope of the log–log plot of K_d vs $[CaCl_2]$ is smaller than expected from Eq. (15). It does not appear that $Ca^{2+} \leftrightarrow Ba^{2+}$ is the only ion-exchange process. This is because the loading of Ba^{2+} is large in comparison with the charge or ion-exchange

TABLE 1

Chemical Compositions of Different Anomalous Al^{3+}-Substituted Tobermorites

Sample	Composition	Al content (%)[a]	Calculated cation exchange capacity[b] (meq/g)
1	$Ca_{5.0}Na_{0.036}Al_{0.060}Si_{5.93}O_{16}(OH)_2 \cdot 4.91H_2O$	1	0.048
2	$Ca_{5.0}Na_{0.218}Al_{0.30}Si_{5.72}O_{16}(OH)_2 \cdot 5.00H_2O$	5	0.397
3	$Ca_{5.0}Na_{0.284}Al_{0.60}Si_{5.41}O_{16}(OH)_2 \cdot 5.50H_2O$	10	0.785
4	$Ca_{5.0}Na_{0.520}Al_{0.90}Si_{5.10}O_{16}(OH)_2 \cdot 5.79H_2O$	15	1.16
5	$Ca_{5.0}Na_{0.680}Al_{1.20}Si_{4.81}O_{16}(OH)_2 \cdot 6.42H_2O$	20	1.52

[a] Defined by [Al/(Al + Si)} mole ratio.

[b] Based on the Al content or Al^{3+} substitution.

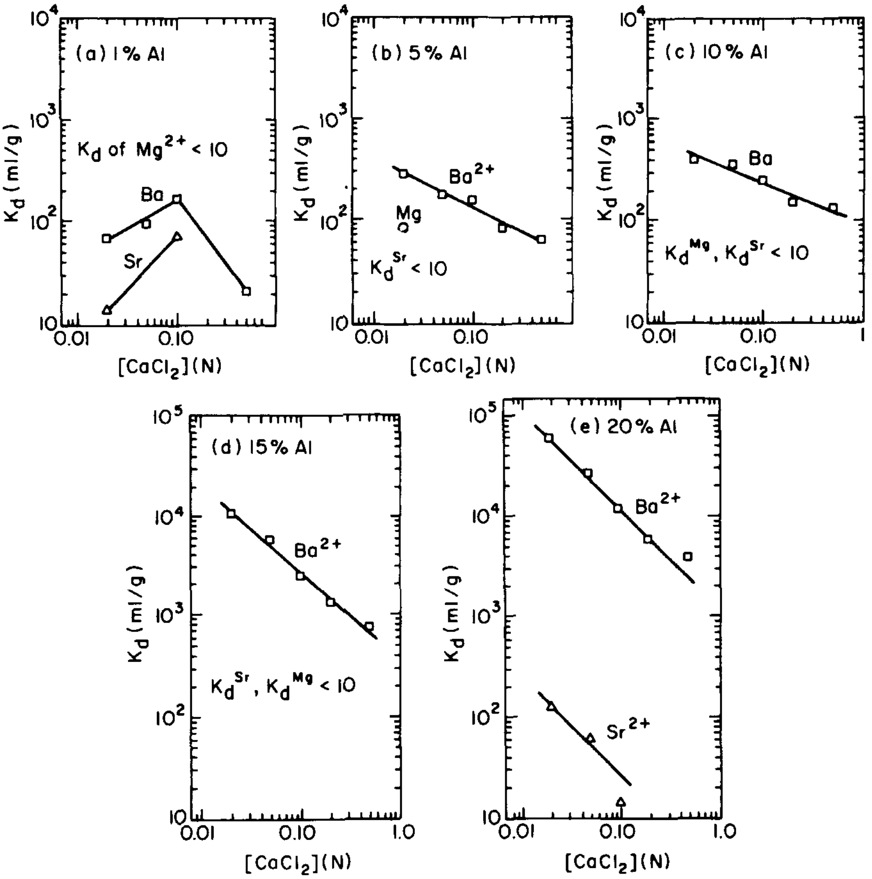

FIG. 1 K_d values for alkaline earth metal ions as a function of $CaCl_2$ concentration in tobermorites with different substitutions: (a) 1% Al, (b) 5% Al, (c) 10% Al, (d) 15% Al, and (e) 20% Al.

ity (Table 1). The slope of the plot is about −1 on tobermorites, with Al^{3+} substitution greater than 15%. This indicates the "ideal" ion-exchange (one divalent ion for another) process on tobermorites.

Selectivity for Alkaline Earth Metal Ions in NaCl Solution

In NaCl solutions, the selectivity is much different from that of $CaCl_2$ solutions. A high selectivity for Mg^{2+} was observed in tobermorite with low substitutions: $Mg^{2+} > Ba^{2+} > Sr^{2+}$ in a low concentration of NaCl (Fig. 2a, b). The selectivity for Mg^{2+} decreased with an increase in Al^{3+}

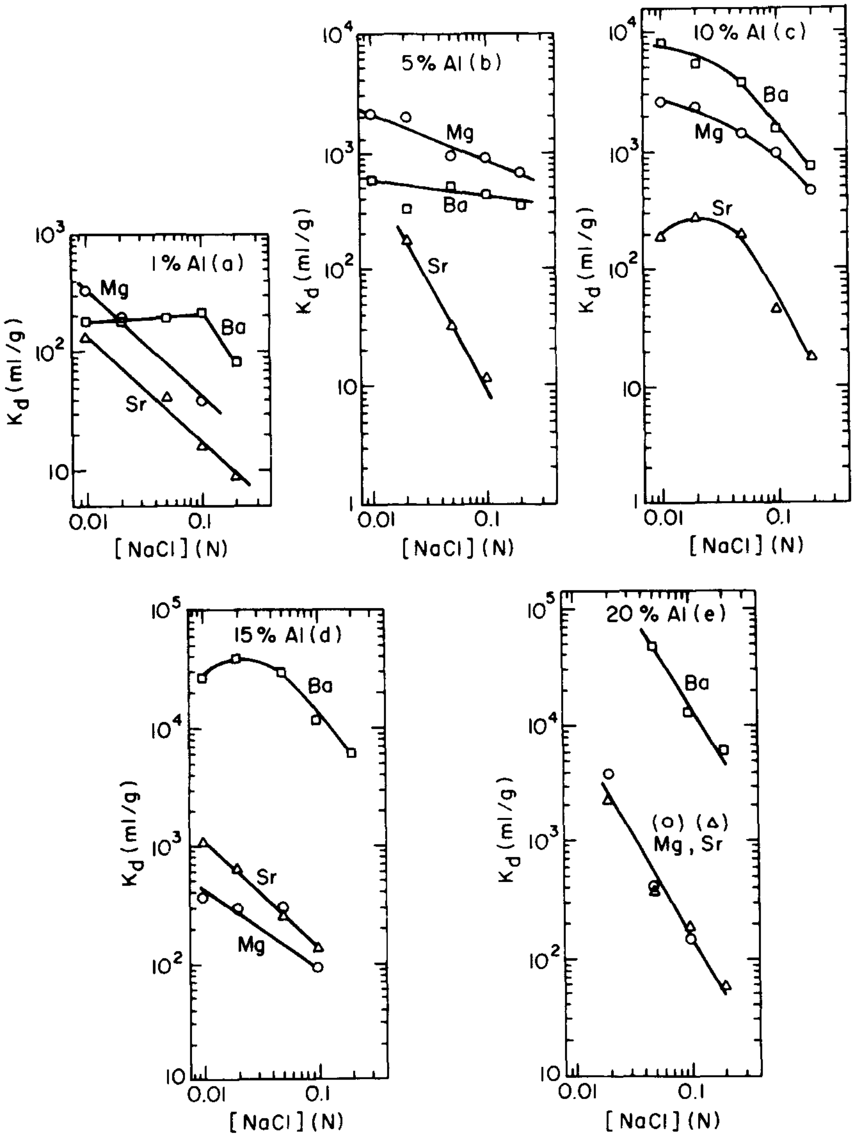

FIG. 2 K_d values for alkaline earth metal ions as a function of NaCl concentration in tobermorites with different substitutions: (a) 1% Al, (b) 5% Al, (c) 10% Al, (d) 15% Al, and (e) 20% Al.

substitution, as can be seen from the following selectivity sequences: $Mg^{2+} > Ba^{2+} > Sr^{2+}$ for 5% Al (Fig. 2b), $Ba^{2+} > Mg^{2+} > Sr^{2+}$ for 10% Al (Fig. 2c), $Ba^{2+} > Sr^{2+} > Mg^{2+}$ (Fig. 2d), and $Ba^{2+} \gg Sr^{2+} = Mg^{2+}$ (Fig. 2e). Higher K_d values for the three cations were observed in NaCl solution than in $CaCl_2$ solution on all tobermorites. The log–log plot of K_d vs [NaCl] did not show a slope of -2 for these cations, which is expected from the "ideal" $2Na^+ \leftrightarrow M^{2+}$ ion-exchange process, except for the 20% Al^{3+}-substituted sample. The 5% Al^{3+}-substituted sample also showed a slope of -2 for Sr^{2+} exchange. These results suggest that some of the ion-exchange sites available for these cations in NaCl solution may be the loosely bound Ca^{2+} between the layers. The alkaline earth metal cations are stoichiometrically exchanged with Na^+ in the tobermorite with 20% Al^{3+}-substitution.

Selectivity for Co^{2+} and Ni^{2+}

Co^{2+} was found to be more selective than Ni^{2+} on 15 mol% Al-substituted tobermorite (Fig. 3). The ion-exchange ideality was confirmed for

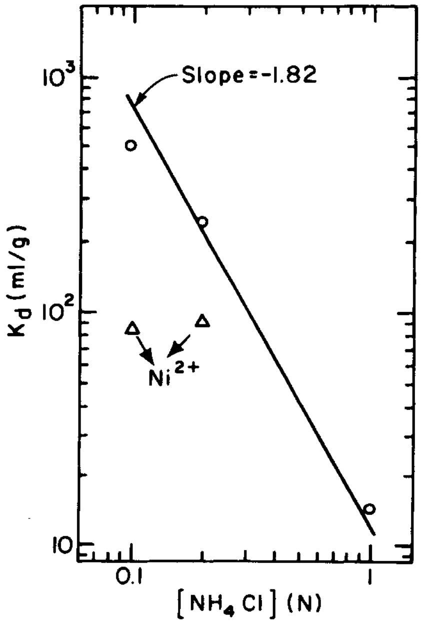

FIG. 3 Log-log plot of K_d for Ni^{2+} and Co^{2+} vs $[NH_4Cl]$ on 15% substituted tobermorite.

Co^{2+} but not for Ni^{2+} because of the latter's low selectivity in NH_4^+ solutions. NH_4^+ has the same ionic radius as K^+, and the former may have been selectively adsorbed by tobermorite. The low Ni^{2+} selectivity may also have been caused by the formation of $Ni(NH_3)_x$ species. As a result, K_d values for Ni^{2+} were lowered in a relatively concentrated NH_4Cl solution.

Very high K_d values for Co^{2+} and Ni^{2+} were observed on xonotlite and tobermorites in $Ca(OOCH_3)_2$ solution in comparison with NH_4Cl solution (Figs. 4 and 5). However, these materials showed nearly the same selectivity toward Co^{2+} (Fig. 4) and Ni^{2+} (Fig. 5), respectively. Since only C sites are available in xonotlite, these ions can only be exchanged with Ca^{2+} in these sites. On the other hand, all three sites can exchange from the 15% Al-substituted tobermorites.

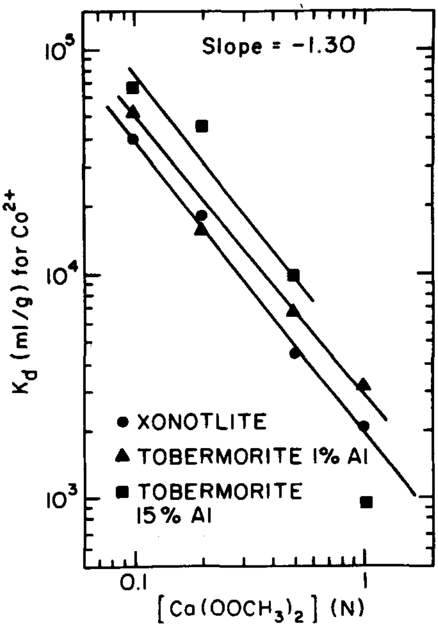

FIG. 4 K_d values for Co^{2+} on xonotlite and tobermorites with 1 and 15% Al^{3+} substitutions in $Ca(OOCH)_3$ solution.

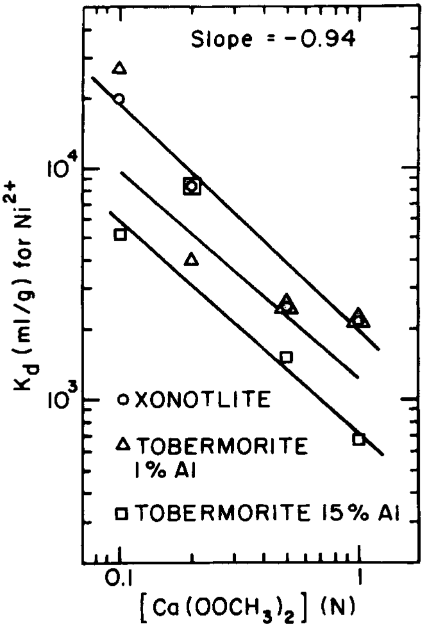

FIG. 5 K_d values for Ni^{2+} on xonotlite and tobermorites with 1 and 15% Al^{3+} substitutions in $Ca(OOCH_3)_2$ solution (lines are drawn to indicate approximate slopes).

CONCLUSION

Exchange sites available for cations in Al-substituted tobermorites are different depending on the coexisting cations and anions, ionic strength, and the extent of Al^{3+} substitution. The complex ion-exchange behavior of these phases can only be deciphered by further extensive studies involving the measurement of the ion-exchange isotherms with different media and at various total normalities.

ACKNOWLEDGMENT

This research was supported by the Separation Processes Program, Division of Chemical and Process Engineering, National Science Foundation, under Grant CBT-8619064.

REFERENCES

1. S. Komarneni, D. M. Roy, and R. Roy, *Cem. Concr. Res.*, *12*, 773–780 (1982).
2. S. Komarneni and M. Tsuji, *J. Am. Ceram. Soc.*, *72*(9) 1668–1674 (1989).
3. S. Komarneni, R. Roy, and D. M. Roy, *Cem. Concr. Res.*, *16*, 47–58 (1986).
4. S. Komarneni, E. Breval, D. M. Roy, and R. Roy, *Ibid.*, *18*, 204–220 (1988).
5. O. P. Shrivastava and F. P. Glasser, *J. Mater. Sci. Lett.*, *4*, 1122–1124 (1985).
6. O. P. Shrivastava and F. P. Glasser, *Reactivity Solids*, *2*, 261–268 (1986).
7. M. Tsuji, S. Komarneni, and P. Malla, *J. Am. Ceram. Soc.*, *74*, 274–279 (1991).
8. R. M. Barrer and J. Klinowski, *J. Chem. Soc., Faraday Trans. 1*, *70*, 2080–2091 (1974).
9. L. V. C. Rees, *The Properties and Applications of Zeolites* (The Chemical Society Special Publications, No. 33), 1979, p. 218.
10. M. Tsuji and S. Komarneni, *Sep. Sci. Technol.*, *26*, 647–659 (1991).

Received by editor September 30, 1991
Revised December 1, 1992