CATION-EXCHANGE PROPERTIES OF (Al + Na)-SUBSTITUTED SYNTHETIC TOBERMORITES

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Abstract—Tobermorite, $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$, is a hydrous calcium silicate that has a layer-type of structure similar to that of the 2:1 clay minerals. In its natural form, tobermorite exhibits little or no exchange for alkali cations; synthetic tobermorites, however, exhibit reversible alkali cation exchange and selective cesium uptake upon a coupled substitution of $(Al^{3+} + Na^+)$ for Si^{4+}. Substituted tobermorites were synthesized using aluminosilicate gels, NaOH, and CaO, in Parr bombs at 175°C for 4 days. Unsubstituted tobermorite was synthesized using quartz and CaO in a Parr bomb at 175°C for 20 hr. Two (Al + Na)-substituted tobermorites showed cation-exchange capacities (CEC) of 77 and 71 meq/100 g, whereas an unsubstituted tobermorite showed a CEC of 12 meq/100 g. The substituted tobermorites exhibited selective Cs exchange from either NaCl or $CaCl_2$ solutions. For example, one substituted tobermorite showed a Cs-exchange coefficient (K_d) of 15,100, whereas unsubstituted tobermorite showed a K_d of only 90 from a 0.02 N $CaCl_2$ solution containing 0.0002 moles/liter CsCl. Exchange isotherms for $Na^+ \rightleftharpoons Cs^+$ showed that Cs^+ is preferred over Na^+ throughout the exchange in the (Al + Na)-substituted tobermorites. This group of cation exchangers is expected to find applications in radioactive waste disposal.

Key Words—Cation exchange, Cation substitution, Cs-exchange, Synthesis, Tobermorite.

INTRODUCTION

A crystal-chemical relationship exists between 2:1 clay minerals and hydrated calcium silicates of the tobermorite group (Taylor, 1950; McConnell, 1954; Taylor and Howison, 1956). Tobermorite, $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$, is a hydrous calcium silicate that has a layer-type of structure (Megaw and Kelsey, 1956; Hamid, 1981). The central part of each layer, equivalent to the octahedral sheet in a clay mineral, may be described as a distorted calcium hydroxide sheet divested of all hydrogen atoms (Taylor and Howison, 1956). This central sheet is coupled on both sides to rows of silicate tetrahedra which are linked into wollastonite-type chains, oriented parallel to the *b*-axis. The SiO_2 chains on either side of the central CaO sheet can be construed as analogous to the tetrahedral sheets in a clay mineral. Thus, tobermorite has a crystal structure similar to that of a 2:1 clay mineral.

The basal spacing of tobermorite varies with water content, similar to the basal spacing of 2:1 clay minerals. Three important crystalline tobermorite phases are known which have basal spacings of about 14, 11.3, and 9.7 Å, depending upon their hydration state (Taylor, 1964).

The dehydration behavior of 14-Å tobermorite (Farmer *et al.,* 1966) is analogous to that of the 2:1 clay minerals; however, unlike the 2:1 clay minerals dehydrated tobermorites do not rehydrate. The dehydration behavior of an 11.3-Å tobermorite depends on the number of tetrahedral cross-links between the

layers. The 11.3-Å tobermorite, containing few if any Si–O–Si bridges between the layers, collapses to 9.7 Å upon heating at 300°C; this variety is designated as 'normal' (Taylor, 1974; El-Hemaly *et al.,* 1977). On the other hand, the 11.3-Å tobermorite, containing numerous Si–O–Si bridges between the layers, does not collapse to 9.7 Å upon heating at 300°C; this variety is designated as 'anomalous' (Taylor, 1974; El-Hemaly *et al.,* 1977). The presence of numerous Si–O–Si bridges (Wieker *et al.,* 1982) between the layers of anomalous tobermorites was detected by ^{29}Si magic angle spinning-nuclear magnetic resonance spectroscopy (MAS-NMR) (Wieker *et al.,* 1982; Komarneni *et al.,* 1985b). Anomalous tobermorite is similar to the phyllosilicate ganophyllite, which contains Si–O–Si bridges between the layers (Eggleton and Guggenheim, 1986; Guggenheim and Eggleton, 1986; Komarneni and Guggenheim, 1987). Thus, tobermorites resemble 2:1 clay minerals in other characteristics besides crystal structure.

Cation substitution is also possible in tobermorites (Diamond *et al.,* 1966), just as in 2:1 clay minerals. The substitution of Al^{3+} and Fe^{3+} for Si^{4+} in tetrahedral coordination has been shown by solid state MAS-NMR and Mössbauer spectroscopy (Komarneni *et al.,* 1985b; Pannaparayil *et al.,* 1985). Coupled substitutions, such as $(Al^{3+} + Na^+)$ and $(Fe^{3+} + Na^+)$ for Si^{4+} in tobermorites have been discovered to lead to cation-exchange and selectivity properties similar to those of 2:1 clay minerals and zeolites (Komarneni *et al.,* 1982; Komarneni and Roy, 1983, 1985; Pannaparayil *et al.,* 1985). Tobermorites substituted with Al^{3+} or Fe^{3+}, and containing Ca^{2+} as a charge compensating ion, how-

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Table 1. Starting materials, synthesis conditions, and X-ray powder diffraction (XRD) analyses of synthetic tobermorites.

Sample	Starting materials	Synthesis[1] conditions	Expected chemical composition
1. Pure tobermorite	Quartz + CaO	175°C; 20 hr	$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$
2. (Al + Na)-substituted tobermorite	Si-Al gel + CaO + NaOH	175°C; 96 hr	$Ca_5Si_{5.1}Al_{0.9}Na_{0.9}O_{16}(OH)_2 \cdot 4H_2O$
3. (Al + Na)-substituted tobermorite	Si-Al gel + CaO + NaOH	175°C; 96 hr	$Ca_5Si_{5.1}Al_{0.9}Na_{0.9}O_{16}(OH)_2 \cdot 4H_2O$

Sample	Element concentration in solution (%)				XRD analysis
	Si	Al	Ca	Na	
1. Pure tobermorite	0.10	—	0.14	—	11.3-Å tobermorite, anomalous[2]
2. (Al + Na)-substituted tobermorite	0.11	1.05	0.25	53.5	11.3-Å tobermorite, anomalous[2]
3. (Al + Na)-substituted tobermorite	0.10	0.54	0.03	39.2	11.3-Å tobermorite, anomalous[2]

[1] Saturated steam pressure.

[2] Anomalous tobermorite = tobermorite which retains its 11.3-Å basal spacing on heating at 300°C for 20 hr (El-Hemaly *et al.*, 1977).

ever, do not exhibit high exchange and selectivity properties (Komarneni and Roy, 1983, 1985). The objectives of the present investigation were (1) to show that $(Al^{3+} + Na^+)$-substituted tobermorite exhibits cation exchange and Cs-selectivity properties similar to those of 2:1 clay minerals and zeolites and (2) to determine the Na $\leftrightharpoons$ Cs exchange equilibria of these tobermorites.

MATERIALS AND METHODS

Tobermorite syntheses

Synthetic tobermorites were prepared under hydrothermal conditions and are listed in Table 1. An unsubstituted tobermorite of expected composition $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$ was synthesized using quartz (<325 mesh) (<44 μm) and calcium oxide. Two $(Al^{3+} + Na^+)$-substituted tobermorites of expected chemical composition $Ca_5Si_{5.1}Al_{0.9}Na_{0.9}(OH)_2 \cdot 4H_2O$ were synthesized using an aluminosilicate gel, NaOH, and CaO. Hydrothermal syntheses were carried out in Teflon-lined Parr bombs as follows: The starting materials and boiled (to remove any dissolved CO_2), distilled water were loaded into the Teflon cups and the pressure vessels were sealed. The vessels were then heated in an oven at 175°C for different periods, i.e., 20 hr for unsubstituted tobermorite and 4 days for substituted tobermorites. After the hydrothermal treatment, the bombs were cooled and opened, and the solid and solution phases were separated by centrifugation.

Solid and solution analyses

The solid phases were characterized by X-ray powder diffraction (XRD) using a Philips diffractometer and CuKα radiation and by transmission electron microscopy (TEM) using a Philips 420 EM microscope equipped with energy-dispersive X-ray spectrometry (EDX). The solutions were analyzed for Si, Al, Ca, and Na by atomic emission spectroscopy (AES) using a SpectraMetric SpectraSpan III instrument.

Cation-exchange measurements

The total cation-exchange capacities (CEC) were measured as follows: A known weight of tobermorite was washed four times with 0.5 N NaCl to saturate the exchange sites with Na$^+$ followed by washing five times with 0.01 N NaCl to remove the excess NaCl and to prevent hydrolysis of Na$^+$ from exchange sites. The Na$^+$ on the exchange sites was displaced by washing five times with 0.2 N KCl. The solution was collected and analyzed for Na$^+$ by AES, and the total CEC was calculated after making a correction for excess 0.01 N NaCl which was determined by weighing. This procedure is similar to the one described by Jackson (1974). Three replicates were used in these measurements.

Selective Cs exchange by the tobermorites was measured as follows: Fifteen milliliters of 0.02 N $CaCl_2$ or NaCl containing 0.0002 moles/liter CsCl was added to each 30-mg tobermorite sample, and the mixtures were equilibrated for 24 hr at 25°C. Three replicates were used. After equilibration, the solid and solution phases were separated by centrifugation, and the Cs in solution was determined by atomic absorption spectroscopy (AAS) using a Perkin Elmer PE 703 instrument with electrodeless discharge lamp.

Total Cs exchange in equilibrium with displaced Na$^+$ was also determined by constructing exchange isotherms. Twenty milligrams of each substituted tobermorite was equilibrated for 3 days by dispersing it in 20 ml of CsCl solutions containing 26.6 to 333 μg Cs/ml. After equilibration, the solid and solution phases were separated by centrifugation, and the Cs in solution was analyzed by AAS.

The Na $\leftrightharpoons$ Cs exchange equilibria for substituted tobermorites were determined after three days of equilibration with constant amounts of tobermorite, water, and total cations (0.004 N), but with variable proportions of Cs$^+$ and Na$^+$ ions. In these experiments 20 mg of tobermorite containing Na$^+$ ions in exchange sites
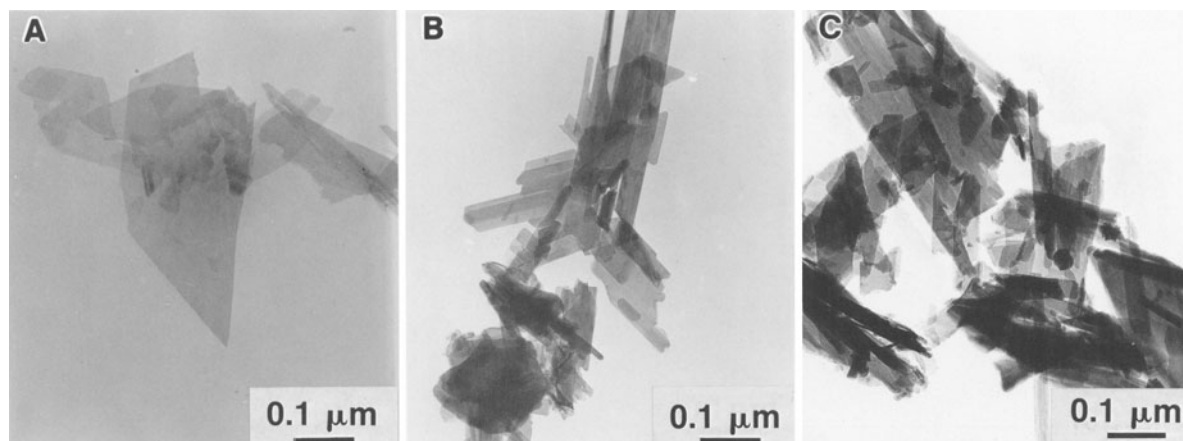
Figure 1. Transmission electron micrographs of synthetic tobermorites: A. Platy crystals of unsubstituted tobermorite (sample 1, Table 1); B, C, lath-like crystals of (Al^{3+} + Na^+)-substituted tobermorite (samples 2 and 3, Table 1, respectively).

was dispersed in 20 ml of solution. After equilibration, the solid and solution phases were separated and the solutions were analyzed for Cs^+ and Na^+ by AAS and AES, respectively.

RESULTS AND DISCUSSION

XRD and TEM analyses of synthetic tobermorites

XRD analyses of synthetic tobermorite solids showed that well-crystallized, "anomalous" tobermorites, both

Figure 2. Lattice-fringe images by high-resolution transmission electron microscopy of (Al^{3+} + Na^+)-substituted tobermorite (sample 2, Table 1) showing layer-type structure having an 11.3-Å basal spacing.

unsubstituted and substituted, were obtained (Table 1). Analyses of the product solutions from the tobermorite syntheses showed that only small amounts of Si, Al, and Ca remained in solution (Table 1); however, 53.5 and 39.2% of the added sodium remained in solution (Table 1) from the (Al + Na)-substituted tobermorite syntheses. These data suggest that the charge balance for the Al substitution for Si in tobermorites was achieved with both Na^+ and Ca^{2+}. Total CEC measurements also (see below) suggest that charge balance was achieved with both Na^+ and Ca^{2+}. The solution analyses coupled with the XRD analyses (Table 1) suggest that tobermorites near the expected chemical compositions (Table 1) were obtained.

TEM analyses showed that single crystals of unsubstituted tobermorite were platy (Figure 1A), whereas those of the (Al + Na)-substituted tobermorites were lath-like (Figures 1B and 1C). These studies confirm earlier observations about tobermorite morphology (Diamond et al., 1966; Mitsuda and Taylor, 1978; Komarneni and Roy, 1985). EDX analyses (figure not shown) of individual crystals showed the presence of all the elements expected from their chemical composition (Table 1). Lattice-fringe imaging by high-resolution TEM showed, as expected, that the tobermorites have a layer-type structure similar to those of clay minerals (Figure 2).

Total cation-exchange and selective cesium-exchange properties

Unsubstituted tobermorite shows only a small total CEC, whereas (Al^{3+} + Na^+)-substituted synthetic tobermorites exhibit much higher CECs (Table 2). The small CEC of the unsubstituted tobermorite results from surfaces and broken bonds, whereas the large CECs of the substituted tobermorite result mainly from the presence of Na^+ in the structure, presumably in the
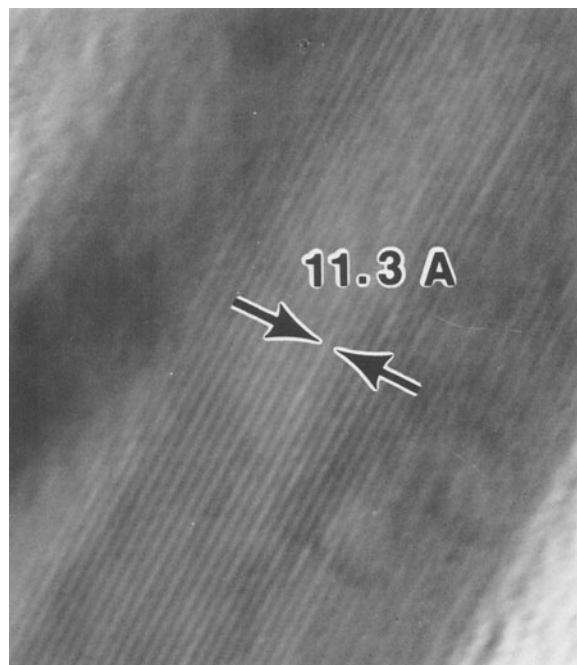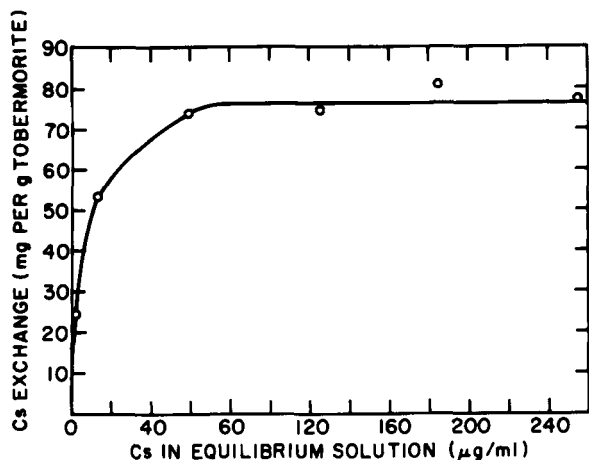
Figure 3. Cs-exchange isotherm of $(Al^{3+} + Na^+)$-substituted tobermorite (sample 2, Table 1).
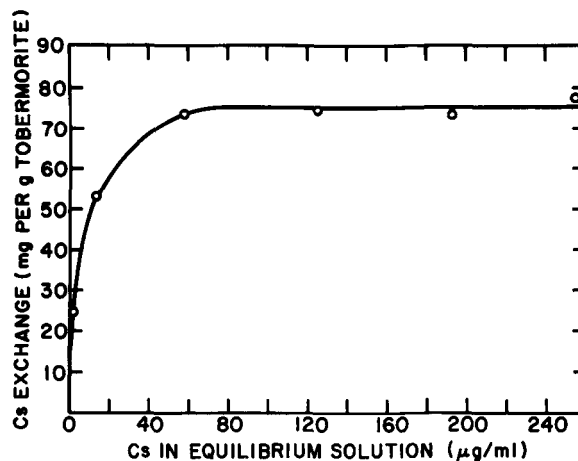
Figure 4. Cs-exchange isotherm of $(Al^{3+} + Na^+)$-substituted tobermorite (sample 3, Table 1).

interlayers. Solid state ^{27}Al and ^{29}Si MAS-NMR data (Komarneni *et al.,* 1985a, 1985b) suggest that the Al^{3+} substitutes for Si^{4+} in the tetrahedral chains as well as in the Si–O–Si bridges across the interlayers. Therefore, the Na^+ ions are probably in the interlayer positions. These tobermorites are "anomalous," which means that numerous Si–O–Si bridges link the adjacent 2:1 layers, thereby forming "interlayer" tunnels along X and zeolite-like sites associated with the tunnel sides where Na^+ ions reside (Komarneni and Guggenheim, 1987), just as in ganophyllite (Guggenheim and Eggleton, 1986). No shrinkage in the basal spacing occurred because of these bridges across the interlayers, and, thus, these tobermorites behaved like many zeolites which also do not shrink significantly upon heating to 300°C. The measured total CECs are only two thirds of that expected on the basis of the Al^{3+} content of the tobermorite. This discrepancy is probably due to the fact that to maintain charge neutrality, some Ca^{2+} must have been substituted in the interlayers. These Ca^{2+} ions are, however, too hydrated to be displaced from the interlayers for steric reasons just as for unsubstituted tobermorite (Komarneni and Roy, 1983, 1985) which contains interlayer Ca^{2+} ions (Hamid, 1981) and for ganophyllite (Guggenheim and Eggleton, 1986). Hence, the CECs are smaller than those calculated from the expected theoretical composition.

The $(Al^{3+} + Na^+)$-substituted tobermorites are highly selective for Cs from both 0.02 N NaCl and $CaCl_2$ solutions (Table 2), similar to zeolites (Ames, 1963), because of steric factors, i.e., the interlayer spacing is equivalent to the thickness of two SiO_4 tetrahedra, and this small interlayer spacing is conducive for the uptake of Cs^+ ions which are less hydrated than Na^+ or Ca^{2+}. Thus, the less hydrated Cs^+ ions are preferentially exchanged over the highly hydrated Na^+ and Ca^{2+} ions. The Ca^{2+} ions are more hydrated than Na^+ ions (Hunt, 1963); hence, Cs was taken up more preferentially from 0.02 N $CaCl_2$ than from 0.02 N NaCl, as indicated by the higher Cs distribution coefficients resulting from $CaCl_2$. The highly hydrated Ca^{2+} ions in the interlayers of unsubstituted tobermorites (Hamid, 1981) are trapped and, hence, not exchangeable (Komarneni and Roy, 1983). Similarly, the extra Ca^{2+} ions substituted along with Na^+ are not readily exchangeable from substituted tobermorites. Charge densities for the various sites in the anomalous tobermorites may also be related to Cs selectivity; this is an area for further investigation. Unsubstituted tobermorites showed no selectivity for Cs because exchange took place only on the surfaces, which have no steric limitations. The Cs-selectivity properties of $(Al^{3+} + Na^+)$-substituted tobermorites are further discussed below because of their potential applications in nuclear waste disposal.

Table 2. Total cation-exchange and selective cesium-exchange properties of synthetic tobermorites.

Sample no.	Sample	Total cation-exchange capacity (meq/100 g)	Cs adsorption K_d[1] (ml/g)	
			in 0.02 N NaCl	in 0.02 N $CaCl_2$
1.	Pure tobermorite	12	20	90
2.	(Al + Na)-substituted tobermorite	77	5000	15,100
3.	(Al + Na)-substituted tobermorite	71	5600	14,400

[1] K_d is a distribution coefficient and is defined as the ratio of the amount of Cs sorbed per gram of sample to the amount of Cs remaining in solution per milliliter.
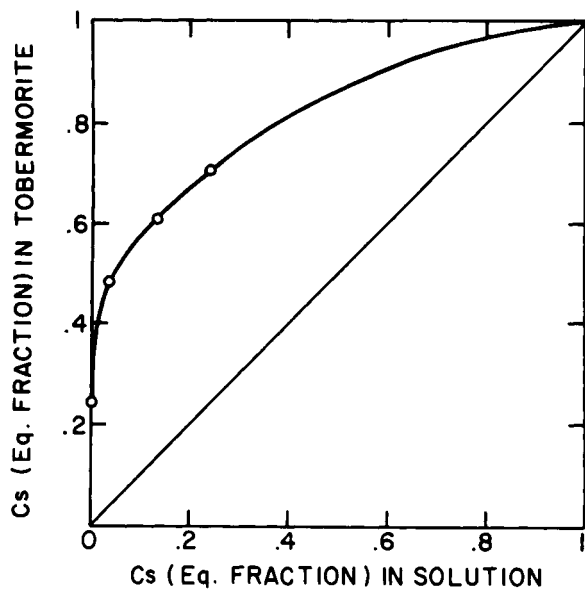
Figure 5.   Na$^+$ ⇌ Cs$^+$ exchange equilibrium for (Al^{3+} + Na$^+$)-substituted tobermorite (sample 2, Table 1).

Cesium exchange from solutions containing only Cs

Figures 3 and 4 are exchange isotherms for Cs for two (Al^{3+} + Na$^+$)-substituted tobermorites. Analyses of displaced Na$^+$ from tobermorite closely matched with the amounts of Cs$^+$ exchanged onto tobermorite, suggesting a stoichiometric exchange. The total Cs-exchange capacities in the presence of displaced Na$^+$ ions are 57.2 and 56.4 meq Cs/100 g for synthetic tobermorite samples 2 and 3 (Table 2), respectively. These
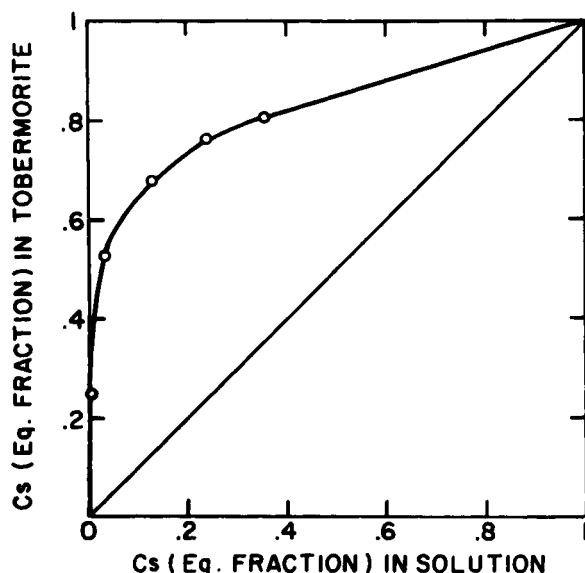
Cs-exchange capacities are slightly smaller than the total (Table 2), because Na$^+$ ions were present in the former equilibrium solution, but not in the latter. These results show that Cs$^+$ exchange for Na$^+$ can proceed almost to the limit of the CEC (Table 2) if much higher Cs$^+$ concentrations are used and if the Na$^+$ concentration is insignificant.

Na$^+$ ⇌ Cs$^+$ exchange equilibria

Cs exchange in systems containing constant amounts of tobermorite, water, and total cations, but variable proportions of Cs$^+$ and Na$^+$ ions was determined (Figures 5 and 6) to find out whether Cs$^+$ is preferred throughout the exchange process (Breck, 1974). The equilibrium equivalent fractions of Cs in tobermorite and in solutions were calculated (Breck, 1974) and plotted as exchange isotherms (Figures 5 and 6) to determine Cs selectivity. The lines at 45° slope (diagonals) in Figures 5 and 6 correspond to an absence of selective exchange for Cs (Breck, 1974). If the isotherm is above the diagonal, the tobermorite exhibits a preference for the entering Cs ion. If the isotherm is below the diagonal, the tobermorite does not prefer Cs$^+$ ions over Na$^+$ ions (Breck, 1974). The exchange isotherms for Cs fall above the diagonal at all concentrations for both (Al^{3+} + Na$^+$)-substituted tobermorites (Figures 5 and 6) suggesting a preference for Cs$^+$ in tobermorites throughout the exchange process. Selective Cs exchange on such tobermorites may be useful in decontaminating circulation water in nuclear reactors and radioactive waste solutions.

ACKNOWLEDGMENT

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Figure 6.   Na$^+$ ⇌ Cs$^+$ exchange equilibrium for (Al^{3+} + Na$^+$)-substituted tobermorite (sample 3, Table 1).

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