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Tobermorites: A New Family of Cation Exchangers

Abstract. *Tobermorites have cation-exchange and selectivity properties intermediate between those of clay minerals and zeolites. Aluminum-substituted tobermorites in particular show high selectivity for cesium. This new group of cation exchangers may find applications in catalysis and in nuclear and hazardous waste disposal.*

Tobermorite, $Ca_5Si_6H_2O_{18} \cdot 4H_2O$, is a naturally occurring hydrous calcium silicate in calc-silicate rocks. Of the various hydrous calcium silicates, the tobermorite group (*1*) is the most important in cement hydration. Isomorphous substitution of aluminum for silicon in the dreirketten of tobermorite has been observed (*2*), and we recently reported cation-exchange and Cs^+-selective properties of the aluminum-substituted tobermorite (*3*). We report here the discovery of tobermorites as a new family of exchangers. Clay minerals and zeolites act as cation exchangers, sorbents, and molecular sieves which have myriad applications in catalysis, nuclear and hazardous waste disposal, and waste-water treatment. Tobermorites have layer structures similar to those of 2:1 clay minerals (*4*), but the structure varies with the chemical composition as well as with the nature of the synthesis (*5*). Wieker *et al.* (*6*) recently elucidated the structures of synthetic tobermorites, using solid-state high-resolution ^{29}Si nuclear magnetic resonance spectroscopy. The chemical composition and structure of tobermorites are important in their cation-exchange and selective properties.

We synthesized tobermorites from many starting materials at 80° to 200°C. Zeolites, such as clinoptilolite from Idaho, phillipsite from Nevada, and Linde 3A, were used as some of the silica-alumina sources. Other materials such as amorphous SiO_2 (−400 mesh); quartz (crystalline SiO_2) (−325 mesh); $Na_2SiO_3 \cdot 9H_2O$; $AlCl_3 \cdot 6H_2O$; and NaOH also were used (Table 1). Teflon capsules were used for synthesis at 85° and 180°C at saturated steam pressure in a pot furnace; polyethylene bottles were used for synthesis at 80°C in an oven; and gold capsules were used at 180° and 200°C in cold-seal vessels under a confining pressure of 30 MPa. The solids were removed from the capsules or bottles and washed with deionized water prior to x-ray diffraction analysis (XRD), scanning electron microscopy (SEM), cation exchange, and cesium sorption measurements. The normal, anomalous, or mixed behavior of the tobermorites was determined by heat treatment at 300°C for 20 hours, after which they were examined by XRD (*5*). Tobermorites are described as normal if the basal spacings decreased to 10 Å or less after heating to 300°C and anomalous if they did not shrink below 11 Å under these conditions. The term "mixed tobermorite" is used for products containing both normal and anomalous tobermorites.

We measured the cation-exchange capacity (CEC) of the various products by using a modified version of the method of Dolcater *et al.* (*7*). A known weight (10 to 50 mg) of each sample was washed twice with 3*N* KCl, then washed three times with 0.01*N* KCl to remove excess KCl and to prevent hydrolysis of K^+ from the exchange sites (a correction was made for excess 0.01*N* KCl, which was determined by weighing); the K^+ was displaced from the exchange sites with four washings of 1*N* CsCl (1/2 hour

Table 1. Cation exchange capacities and selective cesium sorption properties of synthetic tobermorites. Abbreviations: SS, saturated steam; T_{Al}, aluminum-substituted tobermorite; A, anomalous, C, crystalline; PC, poorly crystalline (became amorphous at 300°C); M, mixed; VC, very crystalline as determined by XRD; amor., amorphous; N, normal; ND, none detected.

Sample No.	Initial sample mixture	Temperature (°C); pressure; duration (days) of treatment	Mineralogy by XRD after treatment	Cation exchange capacity (meq/100 g)	Cesium sorption K_d (ml/g) from solution*	
					0.02*N* $CaCl_2$	0.02*N* NaCl
1	420 mg $Na_2SiO_3 \cdot 9H_2O$ + 39.6 mg $AlCl_3 \cdot 6H_2O$ + 76.8 mg CaO	180°; SS; 1	T_{Al} (A, C), calcite†	182‡	4,144 ± 626	2,683 ± 106
2	420 mg $Na_2SiO_3 \cdot 9H_2O$ + 39.6 mg $AlCl_3 \cdot 6H_2O$ + 76.8 mg CaO	85°; SS; 4	T_{Al} (PC), calcite	164‡	756 ± 7	654 ± 9
3	210 mg $Na_2SiO_3 \cdot 9H_2O$ + 5.3 mg kaolinite + 38.4 mg CaO	180°; 30 MPa; 14	T_{Al} (M, VC), calcite	146	14,240	
4	45.9 mg phillipsite + 16 mg amor. SiO_2 + 38.4 mg CaO	200°; 30 MPa; 28	T_{Al} (A, VC)	148‡	20,370 ± 1,985	8,930
5	22.2 mg Linde 3A + 34.8 mg amor. SiO_2 + 38.4 mg CaO	200°; 30 MPa; 28	T_{Al} (A, VC)	158‡	6,328 ± 258	3,670
6	50.7 mg clinoptilolite, Idaho, + 10.4 mg amor. SiO_2 + 38.4 mg CaO	200°; 30 MPa; 28	T_{Al} (A, VC), xonotlite, calcite	80‡	9,150	4,412 ± 157
7	2.22 g Linde 3A + 3.48 g amor. SiO_2 + 3.84 g CaO + 24 g NaOH	80°; SS; 22	T_{Al} (N, PC), calcite	144‡	461 ± 15	484 ± 18
8	5.04 g CaO + 5.4 g amor. SiO_2 + 32 g NaOH	80°; SS; 12	12.6-Å tobermorite (N, VC), calcite	130‡	42	51 ± 2
9	38.4 mg CaO + 49.3 mg quartz (−325 mesh)	200°; 30 MPa; 28	Tobermorite (A, VC), xonotlite	48	120	190
10	38.4 mg CaO + 49.3 mg quartz (−325 mesh)	200°; 30 MPa; 28	Xonotlite (VC), quartz	12	8	ND

*Plus or minus sign denotes standard deviation (*N* weighting) based on three or four replicates. †Calcite is a common constituent of hydrous calcium silicate synthesis. ‡Average of duplicate determinations.

equilibration for each); $[K^+]$ was determined by atomic emission spectroscopy. When NH_4Cl was used to displace K^+ from the exchange sites, lower CEC values were obtained, probably because of H^+ bonding and poor diffusion of NH_4^+ into the structure. We determined whether there was selective cesium sorption by the various tobermorites by adding 10 ml of 0.02N $CaCl_2$ or 0.02N NaCl containing 0.0002N CsCl (Ca^{2+}/Cs^+ or Na^+/Cs^+ equivalent ratio is 100 to 1) to 20 mg of sample, equilibrating for 1 day in glass vials, centrifuging to separate solid and solution phases, and analyzing Cs^+ in solution by atomic absorption spectrophotometry. Cesium sorption is expressed as K_d (in milliliters per gram) values (K_d is a distribution coefficient defined as the ratio of the amount of cesium sorbed per gram of solid to the amount of Cs^+ remaining per milliliter of solution).

The various synthetic tobermorites exhibit CEC values (Table 1) similar to those of vermiculites, higher than those of montmorillonites, but lower than those of most zeolites. Cation exchange was exhibited by both aluminum-substituted tobermorites and by unsubstituted tobermorites.

The 12.6-Å normal tobermorite with Na^+ in the interlayers (Table 1, sample 8) has a CEC of 130 meq per 100 g, whereas the 11.3-Å anomalous tobermorite with Ca^{2+} in the interlayers (Table 1, sample 9) has a CEC of only 48 meq/100 g. This difference in exchange capacity may be due to the nature of the interlayer ions and to the structure of the tobermorite. The less hydrated Na^+ of sample 8 with few or no Si–O–Si bridges between the chains (layers) can be easily displaced, whereas the highly hydrated Ca^{2+} ions from sample 9 cannot be easily displaced because of the numerous Si–O–Si bridges (Fig. 1) between the chains (*6*). Another calcium silicate hydrate, xonotlite, which has a structure similar to that of amphiboles (*4*), exhibits a low CEC of 12 meq/100 g (Table 1, sample 10). We propose that the CEC of xonotlite results primarily from the surfaces and broken bonds.

The aluminum-substituted tobermorites with Na^+ or K^+ in the interlayers exhibit high CEC irrespective of their anomalous, mixed, or normal behavior (Table 1), that is, both in the absence and in the presence of numerous Si–O–Si bridges between the chains. This difference between the aluminum-substituted tobermorites and the unsubstituted anomalous tobermorite may be due to the case with which Na^+ or K^+ is displaced in the former by comparison with the case for Ca^{2+} in the latter. The CEC of these aluminum-substituted tobermorites arises not only from the substitution of aluminum for silicon but also from the interlayer ions that would be present in unsubstituted tobermorites. The CEC values reported here are lower than would be expected from the known composition and structure of tobermorites. This discrepancy may be attributed to at least three factors: (i) incomplete exchange under the conditions used, (ii) variation from ideal composition, and (iii) a dilution effect arising from the presence of calcite (Table 1).

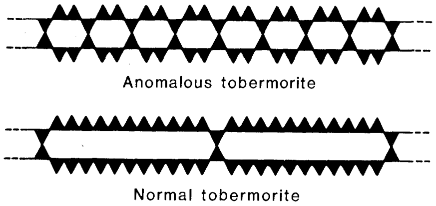

Fig. 1. Double-chain schematic structure in anomalous (numerous Si–O–Si bridges) and normal (few Si–O–Si bridges) tobermorites [after Wieker *et al.* (*6*)].

Unsubstituted tobermorites have little or no selectivity for the large and less hydrated Cs^+ from 0.02N $CaCl_2$ or 0.02N NaCl. On the other hand, aluminum-substituted tobermorites exhibit very good selectivity for Cs^+, that is, high cesium sorption K_d from 0.02N $CaCl_2$ or 0.02N NaCl. For example, sample 1 (Table 1) has a CEC of 182 meq/100 g, and it sorbed 9 meq of cesium per 100 g from 0.02N $CaCl_2$ (the equivalent ratio of CEC to cesium sorbed is 20 to 1) even though the Ca^{2+}/Cs^+ ratio in solution is 100 to 1. Thus, the cesium sorption is in excess of what can be expected from the total exchange capacity of the aluminum-substituted tobermorite and the Ca^{2+}/Cs^+ equivalent ratio in the equilibrating solution. The high selectivity for Cs^+ probably arises from the amount of aluminum-substitution for silicon and the resulting changes in the structure of tobermorite as well as a change in the interlayer ions. Aluminum-substituted tobermorites synthesized at higher temperatures and pressures have greater selectivity for Cs^+ than those synthesized at lower temperatures and saturated steam pressure (Table 1). This difference can be attributed to the greater substitution of aluminum for silicon along with alkali in the structures synthesized at higher temperatures and pressures. Scanning electron microscopy with energy-dispersive x-ray analysis revealed the sorption of cesium by the lath-like or platy crystallites. This type of platy or lath-like morphology is typical of the synthetic tobermorite crystallites (*5*).

Table 2. Comparative cesium sorption by zeolites, clay minerals, and aluminum-substituted tobermorite.

Sample name	Cesium sorption K_d (ml/g) from 0.02N $CaCl_2$
Zeolites	
Clinoptilolite, Idaho	62,000
Phillipsite, Nevada	42,000
Linde 3A	1,500
Clays	
Montmorillonite, Texas	100
Kaolinite	20
Tobermorite	
Aluminum-substituted tobermorite (highest sorption)	20,000

The aluminum-substituted tobermorites exhibit much higher selectivity for Cs^+ than clay minerals but somewhat lower Cs^+ selectivity than some zeolites (Table 2). The noncrystalline calcium silicate hydrates formed by low-temperature hydration of cements exhibit lower exchange capacities and Cs^+ selectivity than the crystalline aluminum-substituted tobermorites (*8*).

This new group of cation exchangers is thermodynamically favored in cement or concrete and therefore can be incorporated in cement and concrete for use in nuclear as well as hazardous waste disposal. Conceivably, novel ion-exchange cement could be designed for constructing liners for waste landfills. Furthermore, tobermorites with layer-type structures may be useful in catalysis, like the clay minerals, zeolites, and synthetic layered zirconium phosphates.

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