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New tobermorite cation exchangers

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Tobermorite minerals, calcium silicate hydrates substituted with Al^{3+} and alkali, exhibit cation exchange and selectivity properties. The total cation exchange capacities of the Al^{3+} and alkali substituted tobermorites synthesized here range from 128 to 197 meq per 100 g. These substituted tobermorites also have high selectivity for caesium and rubidium. For examples, a tobermorite synthesized from Na_2SiO_3, $AlCl_3$ and CaO has a caesium adsorption coefficient K_d of 7200 while another one synthesized from a zeolite and CaO has a caesium adsorption K_d of 12 850 in 0.02 N $CaCl_2$ containing 0.0002 N CsCl. Pure tobermorites and tobermorites with only Al^{3+} substitution do not exhibit much cation exchange capacity or selectivity because of cation hydration effects and steric factors of tobermorites. The cation exchange and selectivity properties of the Al^{3+} and alkali substituted tobermorites fall between those of clay minerals and zeolites. Unlike clay minerals and zeolites, the new group of cation exchangers is expected to be thermodynamically stable in cement and concrete which have a similar chemical composition. Therefore, the new cation exchangers will be suitable for inexpensive solidification in cement after their use, for example, in decontamination of caesium from low-level nuclear wastes.

1. Introduction

Hydrous calcium silicate minerals occur in a number of localities, primarily as late stage hydrothermal or low temperature alteration products of contact metamorphic calc-silicate rocks, the most well known being those in Crestmore, California [1], Scotland [2, 3], Northern Ireland [4], South Africa [5], Mexico [6], Israel [7] and Japan [8]. Through relatively rare in nature, they play an extremely important role in the hydration reactions of cements [9] where the hydration products range from low temperature poorly crystalline calcium silicate hydrates (C–S–H) to well-crystallized stoichiometric mineral phases. The compositions of the latter crystalline hydrous calcium silicates were shown in the $CaO–SiO_2–H_2O$ system [9]. Of these, the tobermorite group of calcium silicates is perhaps the most important in cement hydration, for it forms the basis of most autoclaved concrete products.

Tobermorite, a rare hydrous calcium silicate mineral ($Ca_5Si_6H_2O_{18}\cdot 4H_2O$) was described first by Heddle in 1880. Isomorphous substitution of Al for Si in the dreierketten of tobermorites, has been observed [10, 11]. Tobermorites substituted with aluminium and alkalis have been discovered by us [12–14] to exhibit cation exchange as well as high Cs selectivity.

Thus tobermorites form another family of natural cation exchangers in addition to clay minerals and zeolites. Zeolites and clay minerals form two large families of natural cation exchangers which have been studied by mineralogists for more than 200 years. The new tobermorite cation exchangers exhibit exchange and selective properties intermediate to those of zeolites and clay minerals [13]. The objective of

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TABLE I Cation exchange capacities and selective caesium sorption properties of synthetic tobermorites, natural montmorillonite and the zeolite phillipsite

Sample	Initial sample mixture	Temperature (°C) pressure and duration (days) of treatment	Mineralogy by XRD after treatment	Cation exchange capacity, (meq per 100 g)	Cs sorption $K_{\rm d}^*$ (ml g^{-1}) from solution	
					0.02 N $CaCl_2$	0.02 N NaCl
1	420 mg Na_2SiO_3, $9H_2O$ + 39.6 mg $AlCl_3$, $6H_2O$ + 76.8 mg CaO	180° C; saturated steam; 4 day	Al-substituted tobermorite, (A, C)[†], calcite	185[‡]	4690 ± 667	2848 ± 114
2	210 mg Na_2SiO_3, $9H_2O$ + 19.8 mg $AlCl_3$, $6H_2O$ + 38.4 mg CaO	180° C; saturated steam; 5 day	Al-substituted tobermorite, (A, C), calcite	158	6200	2323 ± 159
3	210 mg Na_2SiO_3, $9H_2O$ + 19.8 mg $AlCl_3$, $6H_2O$ + 38.4 mg CaO	180° C; 30 MPa; 14 day	Al-substituted tobermorite, (M, C), calcite	153	7200	–
4	202 mg Na_2SiO_3, $9H_2O$ + 26.4 mg $AlCl_3$, $6H_2O$ + 38.4 mg CaO	180° C; 30 MPa, 14 day	Al-substituted tobermorite, (M, VC), calcite	136	4550	–
5	222 mg Na_2SiO_3, $9H_2O$ + 9.8 mg $AlCl_3$, $6H_2O$ + 38.4 mg CaO	180° C; 30 MPa, 14 day	Pectolite, plagioclase feldspars	5	ND	–
6	45.9 mg phillipsite, NV + 16 mg amor. SiO_2 + 38.4 mg CaO + 2 mg NaOH	180° C saturated steam; 4½ day	Al-substituted tobermorite, (A, VC), calcite	197	11630	5410
7	229.5 mg phillipsite, NV + 80 mg amor. SiO_2 + 192 mg CaO	200° C; 30 MPa; 28 day	Al-substituted tobermorite, (A, C)	162	7140	–
8	64.2 mg clinoptilolite, ID + 38.4 mg CaO	200° C; 30 MPa, 28 day	Al-substituted tobermorite, (A, VC)	139	12850	7370
9	4.59 g phillipsite, NV + 1.6 g amor. SiO_2 + 3.84 g CaO + 24 g NaOH	80° C; saturated steam; 22 day	Al-substituted tobermorite, (PC), calcite	128[‡]	872 ± 18	763 ± 38
10	197.2 mg amor. SiO_2 + 19.6 mg AlOOH + 184.4 mg CaO	200° C; 30 MPa; 28 day	Al-substituted tobermorite, (A, C), xonotlite, calcite	16	130	–
11	2.22 g Linde 3A + 3.48 g amor. SiO_2 + 3.84 g CaO + 2.4 g NaOH	80° C; saturated steam; 120 day	Al-substituted tobermorite, (A, C), calcite	–	2930[‡]	–
12	1.03 g SiO_2 (quartz) + 0.8 g CaO	175° C; saturated steam 19 h	Tobermorite (A, C)	12[‡]	130[‡]	–
13	–	–	Montmorillonite, TX	80	100	–
14	–	–	Phillipsite, NV	270	42000	–

[*] $K_{\rm d}$ is a distribution coefficient and is defined as the ratio of the amount of caesium sorbed per gram of solid to the amount of caesium remaining per millilitre of solution. ND = None detected.

[†] A = anomalous; N = normal; M = mixed; C = crystalline; PC = poorly crystalline (became amorphous at 300° C); VC = very crystalline as determined by XRD.

[‡] Average of duplicate determination ± denotes standard deviation based on 3 or 4 replicates.

this paper is to further elucidate the cation exchange and cation sieve processes in crystalline, substituted tobermorites.

2. Experimental details

2.1. Syntheses of substituted tobermorites

Substituted tobermorites were synthesized using different starting materials such as calcium oxide, quartz, amorphus silica, sodium silicate, clinoptilolite from Idaho, phillipsite from Nevada, Linde 3A and sodium hydroxide as given in Table I. Sodium hydroxide was used as a catalyst in some of the syntheses. The various starting materials were treated for different periods in plastic bottles at 80° C in an oven or in teflon capsules at 175 and 180° C under saturated steam conditions i.e. at the steam curve. Some of the tobermorites were, however, synthesized at 180 or 200° C in gold capsules under a confining pressure of 30 MPa in cold seal vessels. Upon completing the syntheses, the samples were separated from the containers and washed with deionized water to remove all the soluble ions.

2.2. Characterization of tobermorites

The synthetic tobermorites were primarily characterized by powder X-ray diffraction (XRD) using a Philips APD-3600 X-ray diffractometer with Cu$K\alpha$ radiation. The normal, anomalous or mixed behaviour of tobermorites was determined by heating the samples at 300° C for 20 h followed by XRD. The tobermorites are described as normal if the basal spacings decreased to 1.0 nm or less on heating at 300° C and anomalous if they did not collapse below 1.1 nm upon heating at 300° C. The term "mixed tobermorite" applies to tobermorites which show intermediate behaviour i.e. they contain both normal and anomalous tobermorite in comparable amounts. The "mixed tobermorite" term is also applied to the tobermorites which give a broad peak at about 1.05 nm upon heating at 300° C [15]. The crystalline nature was also determined by XRD.

Some of the tobermorite samples were characterized for their particle size, shape and chemistry by scanning electron microscopy using an ISI-DS130 instrument with energy dispersive X-ray (EDX) analysis. A few tobermorites were characterized by infrared spectroscopy. Infrared absorption measurements were made on KBr pellets containing about 2% of sample using a Perkin Elmer PE 283B double-beam spectrometer with a KBr pellet in the reference beam.

2.3. Cation exchange and selective sorption measurements

Cation exchange capacities were measured by using a method as described by Komarneni and Roy [13]. Briefly, the method is as follows. About 20 to 30 mg of each sample was washed twice (equilibration time is 30 min for each washing) with 1 N KCl to saturate all the exchange sites with K^+, followed by washing the excess KCl with 0.01 N KCl to prevent hydrolysis (a correction was made for excess 0.01 N KCl which was determined by weighing), displacing the K^+ from the exchange sites with four washings (30 min equilibration time per washing) of 1 N CsCl. The displaced K^+ was determined by atomic emission spectroscopy using a Spectra-Metrics SpectraSpan III instrument.

Selective Cs or Rb sorption by the various tobermorites, phillipsite from Nevada and montmorillonite from Texas were determined by adding 10 ml 0.02 N $CaCl_2$ or NaCl solution containing 0.0002 N CsCl or RbCl to 20 mg of sample, equilibrating for 1 day in glass vials, separating the solid and solution phases by centrifugation and analysing Cs or Rb in solution by atomic absorption spectroscopy using a Perkin Elmer PE 703 instrument with electrodeless discharge lamps.

3. Results and discussion

3.1. Synthetic tobermorites

Fig. 1 depicts portions of X-ray diffractograms of some of the synthetic tobermorities prepared for this investigation. The crystallinity of the tobermorites varied with temperature and duration of synthesis i.e. higher temperatures and/or longer duration resulted in increased crystallinity (Fig. 1 and Table I). Tobermorites crystallized with all the starting materials except in the case of Sample 5 (Table I) which resulted in pectolite, $NaCa_2Si_3O_8OH$ and a minor amount of plagioclase feldspars. Calcite is a common contaminant of these tobermorite syntheses (Fig. 1) because of some CO_2 absorption from air.

Infrared spectra of some of the Al-substituted tobermorites and pectolite are given in Fig. 2. These spectra are typical of tobermorites [11, 12, 16] and the spectrum of pectolite is given for comparison. The H_2O band is essentially absent in the case of pectolite sample as can be expected. Sample B in Fig. 2 shows a band at $\sim 1450\,cm^{-1}$ belonging to the CO_3^{2-} group and confirms the presence of $CaCO_3$ in this sample. All the synthetic tobermorites exhibit anomalous or mixed behaviour (Table I). The distinction between normal, anomalous and mixed tobermorites is given in the experimental section. The anomalous behaviour i.e. non-collapse of the 1.13 nm basal spacing upon heat treatment at 300° C is a result of extensive Si–O–Si (Al) bridges in the tobermorite structure [15, 17]. The Si–O–Si (Al) bridges make the structure very rigid just as in the case of the zeolites where the framework remains intact at 300° C. The aluminium and alkali substituted tobermorites are almost always anomalous or mixed [15].

Scanning electron microscopy of some of the substituted tobermorites revealed platy or lath-like morphology (Figs. 3 and 4) as has been found before [11, 15, 16]. The platy tobermorite in Fig. 3 was synthesized with a lower amount of Al than the lath-like tobermorite in Fig. 4 Tobermorite synthesized from clinoptilolite containing a substantial amount of Al also showed lath-like morphology. Thus, there may be a relationship between the aluminium content of the tobermorite and its crystal morphology. This particular point, however, needs to be investigated further.

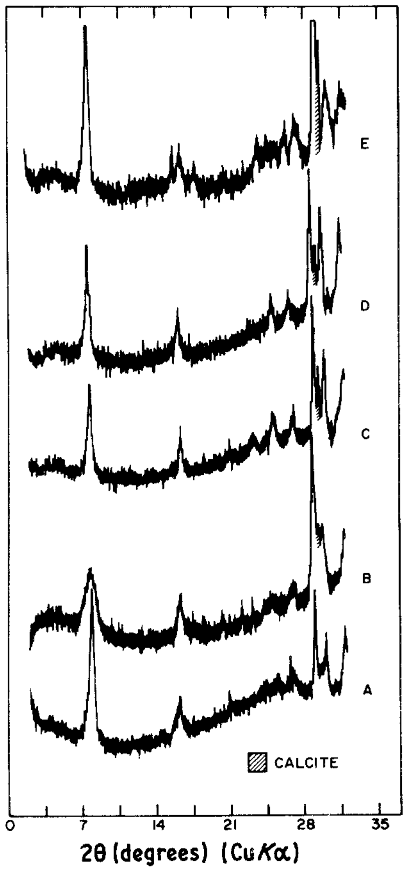

Figure 1 X-ray diffractograms of synthetic tobermorites: (A) quartz + CaO at 175° C/19 h (sample 12 in Table I); (B) Phillipsite + amporphous silica + CaO + NaOH at 80° C/22 day (sample 9 in Table I); (C) Linde 3A zeolite + amorphous silica + CaO + NaOH at 80° C/120 day (sample 11 in Table I); (D) Na_2SiO_3 + $AlCl_3$ + CaO at 180° C/4 day (sample 1 in Table I); (E) Clinoptilolite + CaO at 200° C/30 MPa/28 day (sample 8 in Table I).

3.2. Cation exchange capacities of tobermorites

Tobermorites substituted with aluminium and alkali exhibit cation exchange capacities of 128 to 197 meq per 100 g while tobermorites without any substitutions and with only aluminium substitution have small exchange capacities of 12 and 16 meq per 100 g respectively (Table I). These cation exchange capacities would have been slightly higher had there been no calcite in these tobermorites. The high cation exchange capacities in the aluminium and alkali substituted tobermorites may be attributed to the unhindered exchange of Na and/or K alkali from the structure, while in the Al-substituted tobermorite the exchange of highly hydrated calcium ions is hindered because of steric factors. The negative charge sites in the tobermorite structure arise from the isomorphous

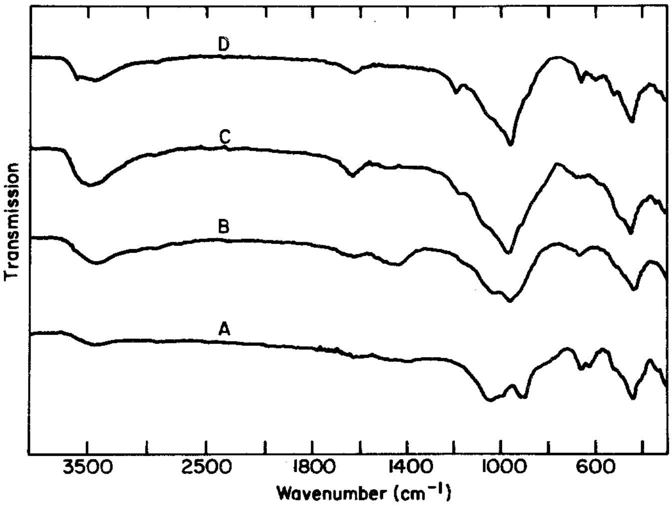

Figure 2 Infrared spectra of: (A) pectolite synthesized from Na_2SiO_3 + $AlCl_3$ + CaO (sample 5 in Table I); (B) Tobermorite synthesized from Na_2SiO_3 + $AlCl_3$ + CaO (sample 1 in Table I); (C) Tobermorite synthesized from clinoptilolite + CaO (sample 8 in Table I); (D) Tobermorite synthesized from amorphous silica + AlOOH + CaO (sample 10 in Table I).

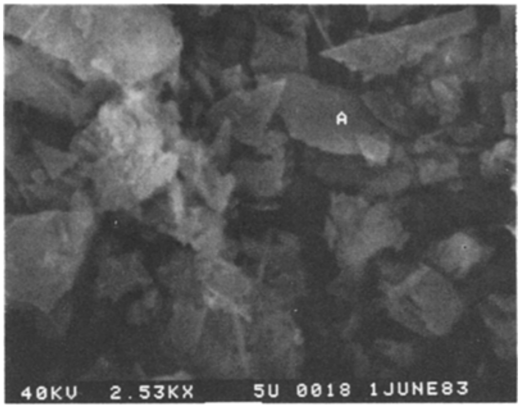

Figure 3 Platy tobermorite synthesized from Na_2SiO_3 + $AlCl_3$ + CaO at 180° C/30 MPa/14 day (sample 3 in Table I). (× 1500)

substitution of aluminium for silicon and are balanced by alkali or Ca^{2+} ions. In the case of unsubstituted tobermorites free Ca^{2+} ions are thought to be present between the layers [18] but these are non-exchangeable (Table I). When tobermorites are substituted by Al^{3+} in the absence of alkali, the negative charge is balanced by Ca^{2+} ions. Since the Ca^{2+} ions are highly hydrated compared to the alkalis, they are not exchangeable just like the interlayer Ca^{2+} in the case of pure tobermorites. The small cation exchange capacities for the unsubstituted tobermorite and the tobermorite substituted with only Al^{3+} (Table I) results probably from the surfaces and broken bonds at the edges. Similarly, the pectolite sample has very little exchange capacity as can be anticipated (Table I). Thus substitution of alkali is essential to generate high cation exchange capacities in the tobermorites.

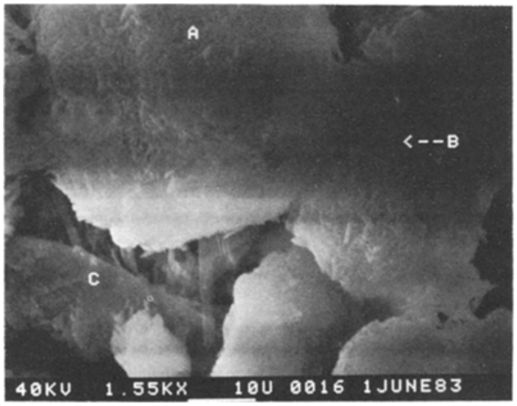

Figure 4 Lath-like tobermorite synthesized from Na_2SiO_3 + $AlCl_3$ + CaO at 180° C/30 MPa/14 day (same as sample 4 in Table I). The lath-like crystals formed mats marked as A and B. (× 930)

The cation exchange capacities of the Al^{3+} and alkali substituted tobermorites fall in between those of clay minerals and zeolites (Table I). Interestingly, the structures of tobermorites can resemble either clay minerals or zeolites depending upon their chemical composition and the nature of synthesis i.e. the structure of tobermorite can be flexible (normal) just as in the case of clay minerals, or rigid (anomalous) just as in the case of zeolites. For this reason, the tobermorite family of cation exchangers is extremely fascinating from a scientific point of view in addition to their anticipated practical uses in nuclear waste disposal, waste water treatment and possibly in catalysis.

3.3. Cation selectivity of tobermorites

The Al and alkali substituted tobermorites selectively adsorb Cs from 0.02 N $CaCl_2$ or NaCl but not the unsubstituted or aluminium alone substituted tobermorites (Table I). The selectivity of Al and alkali substituted tobermorites for Cs from 0.02 N $CaCl_2$ solution is greater than from 0.02 N NaCl which again indicates that the Ca^{2+} ion is too hydrated to diffuse to the negative sites in the tobermorite structure (Table I). The aluminium and alkali substituted tobermorites are also selective for Rb from 0.02 N $CaCl_2$ containing 0.0002 N RbCl. For example, Samples 7, 9 and 10 have Rb adsorption K_d of 4650, 660 and 80 respectively. In general, aluminium and alkali substituted tobermorites synthesized at higher temperatures exhibited higher selectivity for Cs (Table I). The extent of aluminium substitution appears to be greater at higher temperatures and pressures [19] and thus the Cs selectivity may be related to the extent of aluminium substitution. The caesium selectivity is related to both the aluminium and alkali substitution while the cation exchange is mainly connected with the alkali substitution in the tobermorite structures. Substitution of alkali is possible within the tobermorite structure without the substitution of Al and that is why total cation exchange capacity is not related to the Al content [13] but Cs selectivity is closely related to the amount of Al substitution possibly because of steric factors. Figs. 5 and 6 show the EDX analysis of the Cs-saturated tobermorites. Both the plate-like (Figs. 3 and 5) and lath-like (Figs. 4 and 6)

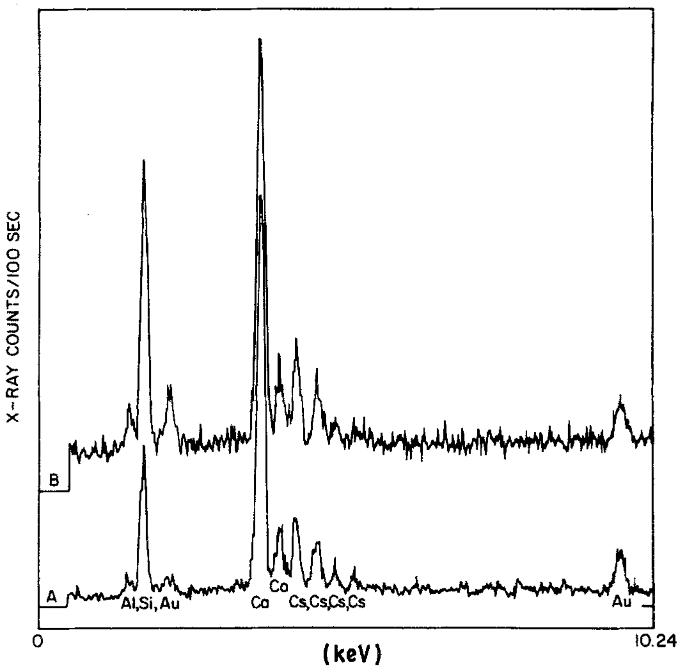

Figure 5 EDX analyses of platy tobermorite (Fig. 3) exchange saturated with Cs. (A) Selected area scan of plate marked A in Fig. 3; (B) Total area scan of Fig. 3.

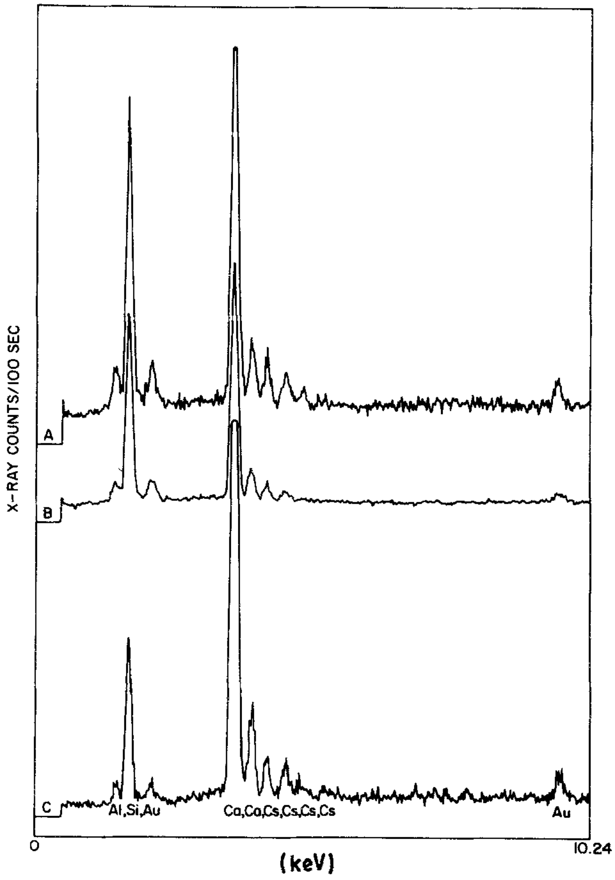

Figure 6 EDX analyses of lath-like tobermorite (Fig. 4) exchange saturated with Cs. (A) Area scan of mat marked A in Fig. 4; (B) Spot scan of prismatic grain marked B in Fig. 4; (C) Spot scan of plate marked C in Fig. 4.

tobermorites show the presence of Cs in their structures. Thus, EDX analysis further confirms the Cs selectivity as well as the cation exchange behaviour of aluminium and alkali substituted tobermorites. The results presented here show that the new tobermorite cation exchangers are an interesting family of exchangers and further research is essential to understand more about their exchange and selectivity properties. Since the tobermorites are essentially calcium silicate hydrates, this new group of exchangers, unlike the clay minerals and zeolites, are expected to be thermodynamically stable in cement. Therefore, these exchangers can be used for caesium decontamination from low-level nuclear wastes and then can be solidified in cement for the immobilization and long-term disposal of low levels of caesium.

4. Conclusions

Tobermorites substituted with Al^{3+} and alkali exhibit high cation exchange capacities and high selectivity for less hydrated monovalent cations such as caesium and rubidium. On the other hand, unsubstituted tobermorites and tobermorites with substitution of only aluminium exhibit only small exchange capacities and little or no selectivity for ions such as caesium and rubidium. Cation hydration and steric factors of tobermorite play a key role in the total exchange capacity as well as the cation selectivity of the substituted tobermorites. The cation exchange and selectivity properties of substituted tobermorites fall between those of clay minerals and zeolites.

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