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TECHNICAL NOTE

Intrinsic Sorption Potential of Aluminum-Substituted Calcium Silicate Hydroxy Hydrate for Cesium-137

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The sorption capacity of synthetic calcium silicate hydrate $Ca_5Al_xSi_{6-x}O_{18}H_{24}\cdot nH_2O$ *(where* $x = 0.025$*) for* Cs^{137} *has been investigated at 25°C using the radiometric method.* Cs^{137} *uptake at different concentrations has been investigated under uniform conditions at various time intervals. The material exhibits the capacity to uptake* Cs^{137} *from tracer solutions. Cs sorption has been studied with pure Cs solution and at 1000 to 5000 times concentration of sodium ions as the competing cation.* ADVANCED CEMENT BASED MATERIALS 1995, 2, 80–83

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Several cement based formulations have been suggested for immobilization of nuclear waste [1–5]. The exact mechanism of immobilization is, however, complex and still unknown. Long-term management of nuclear waste involves conversion of Cs and Sr into aluminosilicate in suitable matrix [6–8]. The interpretation of cation uptake in cement matrix becomes rather difficult because the uptake is not exclusively due to the clay or zeolite type purely thermodynamic cation exchange process. It is also associated with the simultaneous precipitation of some complex silicate species due to the highly alkaline nature of hydrated cement mixtures. In the recent past, several articles have appeared with thermodynamic and kinetic data on uptake reaction of various cations onto the cement phase which is identical to mineral 11-Å tobermorite, a calcium silicate hydrate close to $Ca_5Si_6O_{18}H_2\cdot nH_2O$. Komarneni and Roy [3] have reported its Cs selectivity in the presence of various competing alkali metal and alkaline earth cations. Shrivastava and Glasser [9] have investigated its uptake behavior for several divalent cations. Use of naturally occurring clay minerals like vermiculite has been extensively studied with actual rad wastes. Vermiculite has shown remarkably higher pick-up for radioactive Cs [10]. The reports on Cs selectivity of 11-Å tobermorite have prompted us to evaluate this material for its potential in immobilization of Cs^{137}. The radiochemical data on Cs uptake may also be useful in solving the complex mechanism of ion exchange and cation uptake reactions of tobermorite in particular and other calcium silicate minerals in general.

Experimental

Phase-pure tobermorite appropriate composition (98 to 99% pure) has been synthesized using the hydrothermal method described by Kalousek [11]. The calculated amounts of lime, silica, and alumina were weighed to keep the molar ratio Ca:(Si + Al) equal to 0.8. The products have been characterized by chemical analysis, powder X-ray diffraction between glancing angle $2\theta = 5$ to 80° using Ni-filtered CuK radiation on a Phillips PW-1820 diffractometer. The morphology of tobermorite crystals has been examined with a Phillips 420 TEM microscope. The Cs uptake at different concentrations was followed by the radiometric method: the inactive $CsNO_3$ solution was spiked with Cs^{137} tracer, a β and γ emitter with a half-life of 30 years. The pick-up kinetics were studied after contacting the exchangers with the above solutions for different time periods, and liquid aliquots were withdrawn, centrifuged, and counted for Cs^{137}. The clear solution free from partic-

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ulate matter was counted using a Tl-activated NaI scintillation counter.

Results and Discussion

The phase-pure Al-substituted 11-Å tobermorite was characterized by its typical powder X-ray diffraction pattern, which matches in intensities and positions with the JCPDS file [12]. The resulting product gives 22 reflections with *D* values between 113 and 11.5 nm. The product appeared to be free of unreacted $Ca(OH)_2$, SiO_2, and $CaCO_3$. On shaking the sample in water (solid:water = 1:100), the solution gives a pH of 8.5. The electron micrograph shows a high content of platy crystals characteristic of tobermorites [13]. Crawford et al. [14] have reported that the ordinary Portland cement (OPC) has negligible sorption potential for Cs. The hydrated cements have solid mass with complex microporous regimes. The poor sorption potential of OPC for Cs is attributed to the absence of any crystallochemical incorporation of Cs in cement gels. Studies were made to investigate the pick-up behavior of 11-Å tobermorite for Cs^{137} from pure and mixed cationic solutions at room temperature. The study records the sorption potential of 11-Å tobermorite for Cs^{137} in pure and mixed cationic solutions (Na^+ + Cs^+), respectively. The presence of competing Na^+ ions in higher concentration lowers the Cs uptake capacity and the selectivity coefficients to a sizable extent. Tobermorite exhibited 26% Cs pick-up in the presence of 5000 times concentrated Na^+ solution after 24 hours of equilibration, whereas the pickup in pure $CsNO_3$ solution is as

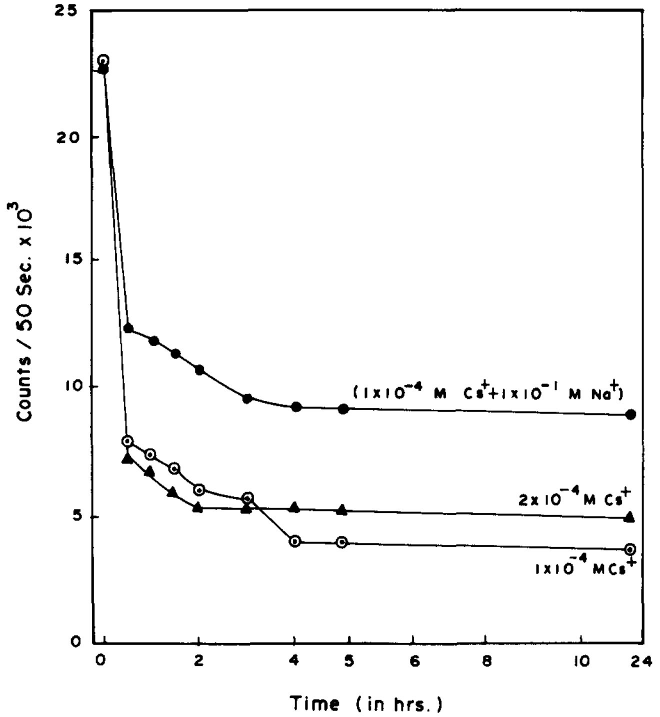

FIGURE 1. Depletion of γ activity of Cs^{137} with time.

TABLE 1. Radiochemical data on concentration dependence of Cs^{137} uptake onto 2.5 mol% Al-substituted tobermorite

	Molarity of Solution (M)							
	2×10^{-4} M Cs^+				1.5×10^{-4} M Cs^+			
	Initial count rate (counts per 50 seconds)							
	22,905 ± 50				20,400 ± 87			
Equilibration time (hours)	**Δ**	**% Cs removal**	**K_d**	**Df**	**Δ**	**% CS removal**	**K_d**	**Df**
0.5	15,714	69	218.52	3.19	8485	41	355.14	1.71
1.0	16,203	71	241.76	3.42	10,972	52	581.88	2.16
1.5	16,981	74	286.65	3.87	10,749	52	556.88	2.11
2.0	17,481	76	322.29	4.22	11,734	57	677.01	2.35
3.0	17,481	76	322.29	4.22	11,798	57	685.77	2.37
4.0	16,481	76	322.29	4.22	12,188	59	742.08	2.48
5.0	17,481	76	322.29	4.22	13,712	66	1025.12	3.05
24.0	17,481	76	322.29	4.22	13,372	65	981.34	2.90
Volume of solution (ml)		100				500		
Amount of exchanger (g)								

Δ = Initial counts − final counts (per 50 seconds).
% Cs removal = (No. of counts sorbed onto exchanger)/(Initial counts in solution) × 100.
K_d = Selectivity coefficient (mg^{-1}) = (Co/Ce_{-i}) A/M, where Co = initial No. of counts; Ce = equilibrium counts in solution; A = volume of solution; and M = mass of exchanger.
Df = Decontamination factor = (initial counts)/(final counts).

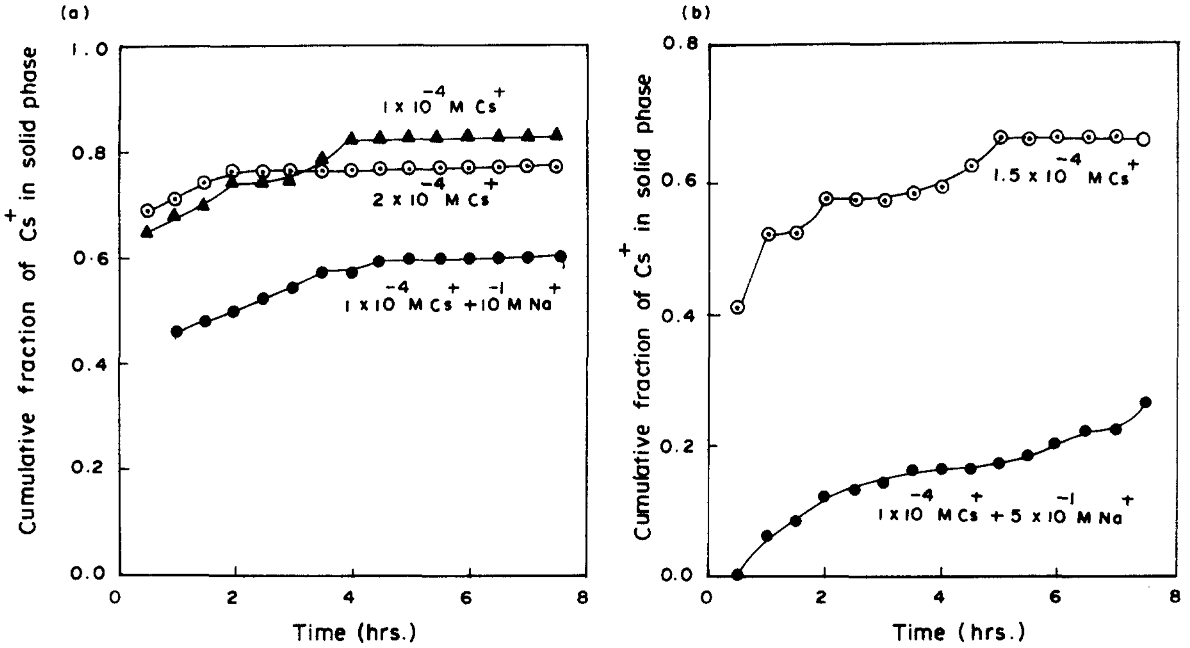

FIGURE 2. Cumulative fraction of Cs exchanged on 2.5 mol% Al-substituted tobermorite.

high as 82%. Table 1 records the time and concentration dependence of Cs uptake in different solutions. Figure 1 compares the depletion of γ activity due to sorption of radiocesium onto tobermorite with and without competing cations. Figure 2 compares the cumulativefraction of Cs in pure solutions with that of mixed cationic solutions containing Na^+ and Cs^+ together. The sorption properties may be attributed to the crystallochemical incorporation of Cs in a layered lattice framework of tobermorite [15–20]. The Cs up-

TABLE 1. Continued

Molarity of Solution (M)											
1.0×10^{-4} M Cs^+				1.0×10^{-4} M Cs^+ + 0.1 M Na^+				1.0×10^{-4} M Cs^+ + 0.5 M Na^+			
Initial count rate (counts per 50 seconds)											
22,905 ± 50				22,905 ± 50				25,414 ± 75			
Δ	% Cs removal	K_d	Df	Δ	% Cs removal	K_d	Df	Δ	% Cs removal	K_d	Df
14,987	65	189.27	2.89	10,501	46	84.66	1.85	1566	0.6	32.88	1.07
15,501	68	209.36	3.09	10,984	48	92.14	1.92	1988	08	42.43	1.08
16,037	70	233.50	3.34	11,489	50	100.64	2.01	3050	12	68.19	1.14
16,853	74	278.47	3.78	12,013	52	110.29	2.10	3150	13	70.74	1.14
17,139	75	297.72	3.97	13,148	57	134.75	2.35	3833	16	88.80	1.18
18,816	82	460.16	5.60	13,411	59	141.26	2.41	4019	16	93.92	1.19
18,816	82	460.16	5.60	13,411	59	141.26	2.41	4482	18	107.06	1.21
18,816	82	460.16	5.60	13,411	59	141.26	2.41	6567	26	174.22	1.35
	100				100				500		

take of tobermorite is also important from the viewpoint of structurally related materials which crystallize as a result of the hydrothermal reaction of lime and silica. The examination of published thermodynamic and kinetic data on sorption of other alkali metal, alkaline earth, and transition metal cations reveals that the uptake in tobermorite is partly due to the ion exchange, along with the simultaneous precipitation of complex silicate species in alkaline medium and the breaking of bonds from the edge of the layered lattice [21]. The characterization of the end products of the sorption or exchange reactions is in progress. The exchange is said to have been caused by the Al^{3+} substitution for Si^{4+}, that is, H_3O^+ subsequently participating in the exchange with Cs ions [10,15]. The simultaneous proportionate release of Ca^{2+} ions in solution to maintain the charge balance, on the other hand, suggests that the calcium of the material is substituted with Cs^+. A more detailed study on the nature and mechanism of Cs sorption onto tobermorite is in progress.

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