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Sr^{2+} uptake and leachability study on cured aluminum-substituted tobermorite–OPC admixtures

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Abstract

Synthetic calcium silicate hydrate (C-S-H), which is similar to 1.1 nm tobermorite mineral, has demonstrated capacity to selectively pick up Sr^{2+} cations from mixed cationic solutions in the presence of 1000 times concentration of Na^+, K^+, Ca^{2+} and Ba^{2+} ions. The selective uptake of Sr^{2+} from mixed cationic solution has been quantified as distribution coefficient (K_d) and decontamination factor (D_f). The mass balance data have been generated from the solution analysis for $Ca^{2+} \leftrightarrows Sr^{2+}$ system after equilibration. The data show that ratio of the amount of Sr^{2+} incorporated in the matrix to the amount of Ca^{2+} released from the tobermorite is approximately equal to 1:1. The position of Al and Si in the aluminum-substituted tobermorite has been characterized by ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MASNMR) spectroscopy. Because 1.1 nm tobermorite is a powder, experiments were carried out on monolithic samples solidified with various amounts of ordinary portland cement (OPC). Leach rate studies were performed to study the retention power of Sr^{2+} in these monoliths. The leach rate of Sr^{2+} decreases drastically due to the addition of 10–40% of tobermorite to the OPC. The Sr^{2+} retention capacity is expressed in terms of meq/100 g of exchanger. The leach rate studies show that Sr^{2+} retention by various tobermorite containing OPC blocks increases with increasing weight percentage of this 1.1-nm Al-substituted tobermorite, which may be used as an additive to make the waste form. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calcium silicate hydrate (C-S-H); Spectroscopy; Admixture; Portland cement; Radioactive waste form

1. Introduction

Inorganic ion exchangers have been studied extensively because of their large-scale applications in separation, processing and synthesis of materials of desired properties [1]. They are superior to organic resins as they are generally resistant to heat and radiations. Recently, calcium silicate hydrate (C-S-H), which is similar to 1.1 nm tobermorite, has been shown to have ion selectivity toward alkali and alkaline earth cations. The chemistry of C-S-H is essentially the chemistry of reaction of calcium hydroxide with silica at high temperature and pressure [2]. Several authors have found that substituted tobermorite behave as a cation exchanger [3–8]. This study was undertaken to explore the possibility of using this material as an additive to ordinary portland cement (OPC) for radioactive waste management. It is well known that Sr^{90} is a hazardous isotope (half-life = 27.7 years) present in the intermediate level waste of nuclear power plants [9,10]. It was therefore thought appropriate to study the Sr^{2+} uptake property of synthetic aluminum-substituted tobermorite and leach rate studies of compact blocks prepared from OPC + tobermorite admixture after 28 days of curing.

2. Experimental

The phase pure exchanger was synthesized by the procedure described by Kalousek [11]. CaO was prepared by calcinations of A.R. grade $CaCO_3$ (99.9% pure) at 1000°C for 5 h. CaO (4.2 g) was added to 13 ml of CO_2 free distilled water and stirred for 3 min. Micronized optical grade quartz (5.7 g; 0.09% nonvolatile with HF) was added and mixed thoroughly using mortar and pestle before addition of sufficient distilled water to keep S/W ratio at 1:5. Calculated quantities of alumina were added to prepare Al-substituted tobermorites. All the reactions were performed at

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saturated steam pressure in Teflon-lined Parr vessel. The Parr bomb was heated at 175°C for 48 h. The product thus obtained was washed several times with decarbonated water and acetone and dried in carbon-dioxide-free air. In water, the product gives a pH of $\sim$8.0. The product was characterized by chemical analysis and powder X-ray diffraction data in the range $2\theta = 5$ to 80°. The morphology of the specimen was also examined using a scanning electron microscope (Phillips 420 TEM) as cited in the literature [12]. The ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance (MASNMR) techniques were used to determine the environment of Al and Si in the hydrothermal product. The Sr^{2+} uptake experiments were carried out using following procedure.

A total of 25 mg of the sample was equilibrated with mixed cationic solutions containing 0.0001 N Sr^{2+} 0.2 N M^{n+} where $M^{n+} = Na^+, K^+, Ca^{2+}$ and Ba^{2+}. After 2 days of equilibration in sealed polythene bottles, the supernatant solution was analyzed for Sr^{2+} by a GBC 902 double-beam atomic absorption spectrophotometer at 460.7 nm using acetylene–nitrous oxide fuel. The amount of Sr^{2+} uptake was determined from the difference in concentration between the reference and the sample. The following procedure was adopted to prepare test specimen (blocks) for leaching [13]. Firstly, the well-crystallized Al-substituted tobermorite powder (in bulk) was saturated with Sr^{2+} by equilibrating it three times in 1000 mg/dm^3 $Sr(NO)_3$ solution for 48 h. This was repeated until Sr^{2+} content in the solid became constant and solution concentration no longer changes. The Sr^{2+} loaded powder was then centrifuged washed and dried in an oven at 110°C. This material was then used to prepare the 10–40 wt.% tobermorite + OPC blocks keeping W/S = 0.6.

2.1. Sr^{2+} leach rate studies

Leaching behaviour of Sr^{2+} from aluminum-substituted tobermorite loaded blocks have been studied at room temperature using standard method described by Hespe [13] under the following test conditions.

(i) The 10%, 20%, 30% and 40% blocks, each of similar dimensions (ht. = 1.2 cm, $r = 0.5$ cm) have been prepared by adding 90%, 80%, 70% and 60% of OPC, respectively, to 10%, 20%, 30% and 40% of 14.4 wt.% alumina-substituted tobermorite. The contents were thoroughly mixed using mortar and pestle keeping total solid/water ratio at 0.6. The slurry was then transferred in plastic moulds to obtain the blocks, which were cured for 28 days in 100% of humidity. The surface area of each block was measured manually with the help of screw gauge.

(ii) Sealed polythene bottles were used as leachant containers.

(iii) The leachant was 25 ml of distilled water at 25°C renewed at each sampling. The sampling was done daily for the first week, weekly for 3 weeks and fortnightly for the rest of period.

3. Results and discussion

After hydrothermal treatment, the aluminum-substituted C-S-H was found to match in intensity and position with the JCPDS file for 1.1 nm tobermorite [14]. The resulting product gave 22 reflections with *d* values ranging from 0.115 to 1.15 nm. The electron micrograph showed high content of platy crystals characteristic of tobermorite [12]. The solid-state ^{27}Al and ^{29}Si (MASNMR) spectra of the

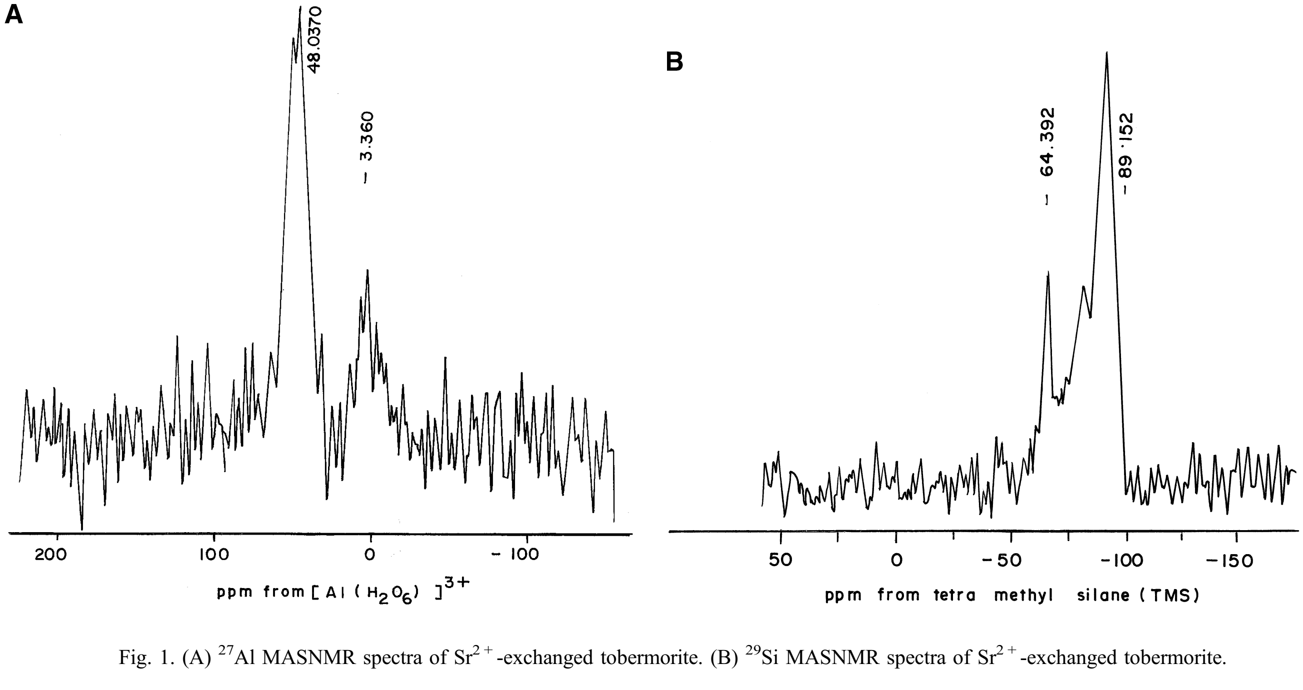

Fig. 1. (A) ^{27}Al MASNMR spectra of Sr^{2+}-exchanged tobermorite. (B) ^{29}Si MASNMR spectra of Sr^{2+}-exchanged tobermorite.

Table 1
Selective uptake data of Sr^{2+} onto different mole percentage aluminum-substituted tobermorite

		Unsubstituted tobermorite		7 mol% Al-substituted tobermorite		16 mol% Al-substituted tobermorite	
Ion pair ($M^{n+}+Sr^{2+}$)	Initial Sr^{2+} (μg/ml)	Δ	% Sr removal	Δ	% Sr removal	Δ	% Sr removal
Na + Sr	22.72	2.8	12.32	3	13.20	3.6	15.84
K + Sr	18.6	Nil	Nil	Nil	Nil	Nil	Nil
Mg + Sr	18.6	2.8	15.05	3.6	19.36	4.5	24.19
Ca + Sr	18.0	2.4	13.33	3.0	16.66	3.8	21.11
Ba + Sr	16.8	0.2	1.19	0.6	3.57	0.8	4.76

Weight of exchange = 25 mg, volume of solution = 25 ml.
Normality of cations = 0.2 N M^{n+} + 0.0001 N Sr^{2+} [M^{n+} = Na^{+}, K^{+}, $Mg^{2+}Ca^{2+}$ and Ba^{2+}].
Equilibration time = 2 days, pH = 7.15.
Δ = initial Sr^{2+} − final Sr^{2+}.
%Sr removal=((Δ × 100)/(initial Sr^{2+})).

postleached tobermorite specimen are shown in Fig. 1(A) and (B). The assignment of the ^{27}Al chemical shifts to tetrahedral coordination is based on earlier investigations [15,16], which shows that tetrahedral coordinated aluminum resonates at 50 ± 20 ppm while octahedrally coordinated aluminum resonates at 0 ± 10 ppm from $[Al(H_2O)_6]^{3+}$ as standard. In this study, two peaks have been observed, one at 48.04 ppm and another at 3.36 ppm. The 48.04 ppm peak is due to the tetrahedral coordination of aluminum while the 3.36 ppm peak appeared due to unreacted aluminate starting material. Previous ^{29}Si MASNMR spectroscopy commonly showed the existence of two different Si sites in aluminum-substituted tobermorite: one is the Si site in SiO_4 tetrahedral chain (Q^2 environment) and another is the Si site in the $\equiv Si-O-Si\equiv$ bridges (Q^3 environment) [17]. ^{29}Si MASNMR spectra of synthetic tobermorite show four different peaks at − 64.39, − 75, − 83.33 and − 89.15 ppm. The resonance at − 64.39 ppm is due to the monomer (Q^0 site) from C_2S and C_3S. Presence of weak signal at − 75 ppm indicates the presence of Q^1 (1Al) site. The strong resonance at − 89.15 ppm is due to the chain middle group (Q^2 site). The middle Q^2 unit is the "bridging" tetrahedron [18,19]. The resonance at − 89.15 and − 83.33 ppm is due to Q^2 (0Al) and Q^2 (1Al), i.e. the presence of no Al and one Al, respectively [20]. The absence of Q^3 and Q^4 lines characteristic of silica gel confirm that tetrahedral aluminum detected with the ^{27}Al MASNMR exists in the C-S-H [21]. The presence of Q^1 signal at − 83.33 ppm corresponds to single-chain silicate anions, while the peak at − 89.15 ppm may be attributed to double-chain silicate anionic framework in the structure of the tobermorite [15]. Table 1 shows that Sr^{2+} selectivity increases with increasing level of aluminum substitution in tobermorite as reported elsewhere [22]. Strontium removal from mixed cationic solution of ($Sr^{2+}Na^{+}$) ranged from 12.3% in unsubstituted tobermorite to 15.84% in 16 mol% aluminum-substituted tobermorite. The alkali metal exchange in tobermorite is a reversible process [23]. The following sequence of blocking effect is observed $Mg^{2+} < Ca^{2+} < Na^{+} < Ba^{2+} < K^{+}$ for different cations on the Al-substituted tobermorites. Thus, Mg^{2+} is the least competitive and K^{+} is the most competitive cation. Cation exchange in the aluminum-substituted tobermorite is mainly from edge and planar surface sites and also from interlayer Ca^{2+} sites [24]. Table 2 shows the mass balance data for $Ca^{2+} \leftrightarrows Sr^{2+}$ system after equilibration. These data show that a little more of calcium is released in the solution than the equivalent amount of Sr^{2+} entering the solid phase leading to ΔCa soln./ΔSr solid ratio equal to 1.00–1.22. This additional release of Ca^{2+} could be due to unreacted portions of calcium which might be present as traces of $Ca(OH)_2$, which on dissolution raises the ΔCa soln./ΔSr solid molar ratio [17]. Fig. 2 shows a comprehensive data profile obtained from five test blocks. The reference block contains only OPC, whereas the other four test specimens

Table 2
Mass balance data on $Ca^{2+} \leftrightarrows Sr^{2+}$ in 7.0 mol % Al-substituted tobermorite

Moles of Ca in solid	Moles of Ca in solution	Moles of Sr in solid	ΔCa soln. /ΔSr solid	Moles of Sr in solution	Equivalent fraction of Sr in solid	Equivalent fraction of Sr in solution
7.76	0.37	0.31	1.19	0.02	0.03	0.05
7.23	0.90	0.88	1.02	0.18	0.10	0.16
6.01	2.01	1.82	1.10	0.56	0.23	0.21
3.51	4.62	4.40	1.05	1.82	0.55	0.28
2.41	5.72	4.68	1.22	2.76	0.66	0.32
1.85	6.28	5.73	1.09	3.68	0.75	0.36
1.35	6.78	6.45	1.05	4.69	0.82	0.40
0.40	7.73	7.70	1.00	5.74	0.95	0.42
0.30	7.93	7.86	1.00	7.06	0.96	0.47

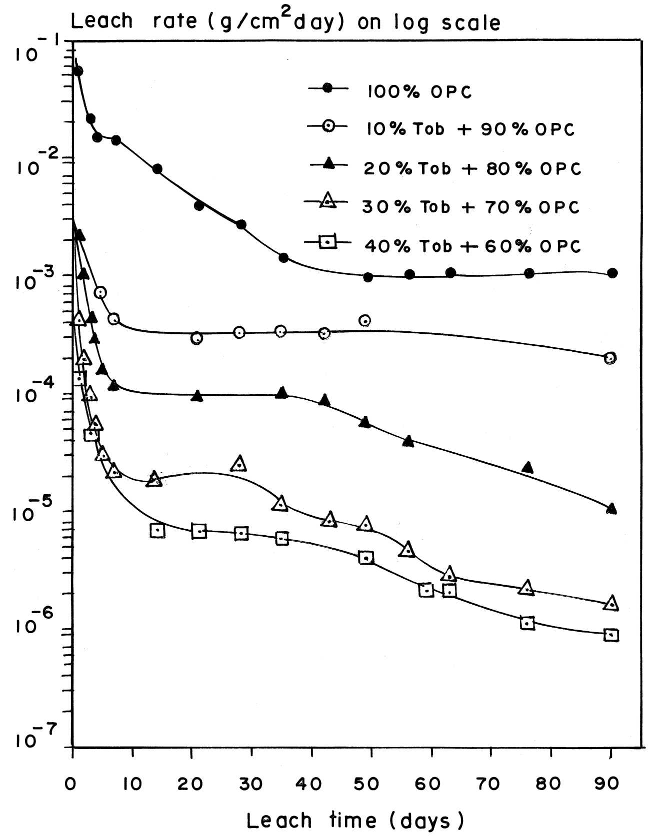

Fig. 2. Leach rate profile of Sr^{2+} from OPC + 14.4 wt.% alumina-substituted tobermorite.

are prepared from the additive and OPC four different proportions (10%, 20%, 30% and 40%). It can be seen that mixing of the synthetic aluminum-substituted calcium silicate hydroxy hydrate with OPC increases the Sr^{2+} retention power of OPC, which by itself shows poor retention of Sr^{2+}. This is demonstrated by the study of leach rate data on the five test blocks. After initial leaching within the first 20 days, there is drastic reduction in release of Sr^{2+} ions from the blocks, which is maintained over a longer period (90 days). The leaching behaviour of cementitious material can be explained as a combination of two processes: surface wash off, which is not diffusion controlled, followed by a semistatic diffusion stage. Leaching in the first few days increases rapidly because equilibrium is established between spaces present in the surface pores of the portland cement and the ions of the solution in the leachant. When Sr^{2+} is leached out from the surface of the block it migrates by longer pathways from the bulk through depleted surface layer before it can enter the solution [25,26]. It is this diffusion-controlled stage that determines the long-term leaching behaviour of the material. The final analysis of the postleached blocks has shown that the strontium content appears to be permanently fixed in the cement matrix. A maximum of 38.20 meq of Sr^{2+}/100 g could be fixed in the blocks.

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References

[1] A. Clearfield, Inorganic Ion Exchange Materials, CRC Press, Boca Raton Press, 1982.

[2] H.F.W. Taylor, Chemistry of Cement, vol. 1, Academic Press, London, 1964, p. 460.

[3] S. Komarneni, D.M. Roy, Pseudomorphism in xonotlite and tobermorite with cobalt (2+) and Nickel (2+) ion exchange for calcium (2+) ion at 25°C, Cem. Concr. Res. 16 (1) (1986) 47–58.

[4] S. Komarneni, E. Breval, D.M. Roy, Reactions of some calcium silicate with metal cations, Cem. Concr. Res. 18 (1988) 204–220.

[5] O.P. Shrivastava, S. Komarneni, E. Breval, Mg^{2+} uptake by synthetic tobermorite and xonotlite, Cem. Concr. Res. 21 (1991) 83–90.

[6] O.P. Shrivastava, S. Komarneni, Cesium selectivity of (Al + Na) substituted tobermorite, Cem. Concr. Res. 24 (3) (1994) 573–579.

[7] N.K. Labhesetwar, O.P. Shrivastava, Iron calcium ion exchange reaction in cement hydration phase 11 Å tobermorite, Ind. J. Chem., Sec. A 27 (11) (1988) 999–1001.

[8] K. Inoue, S. Tsunematsu, H. Yamada, Characteristic of removal of heavy metals by Al-substituted tobermorites, Gypsum Lime 229 (1990) 413–418.

[9] O.P. Shrivastava, P.K. Wattal, T. Verma, Intrinsic sorption potential of Al-substituted calcium silicate hydroxy hydrate for $cesium^{137}$, Adv. Cem. Based Matrices 2 (2) (1995) 80–83.

[10] O.P. Shrivastava, T. Verma, Sr^{2+} sorption and leach rate studies on synthetic calcium silicate hydroxy hydate, Adv. Cem. Based Matrices 2 (3) (1995) 119–124.

[11] G.L. Kalousek, The crystal chemistry of hydrous calcium silicates: I. Substitution of aluminum in lattice of tobermorites, J. Am. Ceram. Soc. 40 (1957) 74–80.

[12] S.A. Hamid, Electron microscopic characterization of the hydrothermal growth of synthetic 11 Å tobermorite ($Ca_6Si_6O_{18}{\cdot}2H_2O$) crystals, J. Cryst. Growth 45 (1979) 421–426.

[13] E.D. Hespe, Leach testing of immobilized radioactive waste solids — a proposal for a standard method, At. Energy Rev. 9 (1) (1971) 1–12.

[14] JCPDS Powder Diffraction File No. 19-1364, 1989.

[15] W. Wieker, A.-R. Grimmer, A. Sinkler, Solid state high resolution Si-29 NMR spectroscopy of synthetic 14 Å, 11 Å, and 9 Å tobermorite, Cem. Concr. Res. 12 (1982) 333–339.

[16] S. Komarneni, R. Roy, D.M. Roy, C.A. Fyfe, G.J. Kennedy, A.A. Bothrer-By, J. Dadok, A.S. Chesnick, ^{27}Al and ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopy of Al-substituted tobermorites, J. Mater. Sci. 20 (1985) 4209–4214.

[17] M. Tsuji, S. Komarneni, Alkali metal ion exchange selectivity of Al-substituted tobermorite, J. Mater. Res. 4 (3) (1989) 698.

[18] G. Engelhardt, D. Michel, High Resolution Solid State NMR of Silicates and Zeolites, Wiley, New York, 1987.

[19] I.G. Richardson, A.R. Brydson, R. Brydson, G.W. Groves, C.M. Dobson, Location of aluminum in substituted calcium silicate hydrate (C-S-H) gels as determined by ^{29}Si and ^{27}Al NMR and EELS, J. Am. Ceram. Soc. 76 (9) (1993) 2285–2288.

[20] M. Tsuji, S. Komarneni, Selective cation exchange in substituted tobermorite, J. Am. Ceram. Soc. 72 (9) (1989) 1668–1674.

[21] P. Faucon, J.C. Petit, Silicon substitution for aluminum in calcium silicate hydrates, J. Am. Ceram. Soc. 82 (5) (1999) 1307–1312.

[22] P.K. Wattal, A.K. Govindan, R. Jahagirdhar, R.R. Chitnis, Evaluation of low and IL radioactive solidified waste forms and packages, IAEA-TECDOC-586, (1990) 157–185.

[23] S. Komarneni, E. Breval, M. Miyake, Cation exchange properties of [Al + Na] substituted synthetic tobermorites, Clays Clay Miner. 35 (5) (1987) 385–390.

[24] O.P. Shrivastava, F.P. Glasser, Ion exchange properties of $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$, J. Mater. Sci. Lett. 4 (1985) 1122–1124.

[25] F.P. Glasser, A.A. Rahman, R.W. Crawford, C.E. McCulloch, M.J. Angus, Immobilization and leaching mechanisms of radwaste in cement based matrices, DOE/RW/83.093, U.K. (1983–1985) 57–68.

[26] I. Plecas, A. Peric, S. Pavolic, Effect of curing time on the fraction of 137 Cs leached from the cement matrix, J. Radioanal. Lett. 200 (1) (1995) 25–29.