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$Ca^{2+} \rightleftharpoons Pb^{2+}$ exchange reaction of calcium silicate hydrate: $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$

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Recently it has been demonstrated that synthetic calcium silicate hydrate $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$ shows cation exchange properties. In this paper we give the mass balance and thermodynamic data of the $Ca^{2+} \rightleftharpoons Pb^{2+}$ exchange which occurs in 1.1 nm tobermorite when placed in dilute Pb^{2+} solutions. The solid and solution phases have been analysed. The free energy of the exchange reaction at room temperature has been calculated. The X-ray powder diffraction data of the exchanged product have been reported. The crystallinity of the exchanger remains intact after ion exchange.

1. Introduction

Silicate minerals both natural and synthetic have been identified as good ion exchangers [1–4]. Cation exchange properties of zeolites, clays and other minerals can be explained on the basis of their typical anionic framework. Recently it has been pointed out that calcium silicate hydrates exhibit remarkable ion exchange capacity towards a series of cations. Roy *et al.* [2] first investigated calcium $\rightleftharpoons$ caesium ion exchange reaction of 1.1 nm tobermorite; a mineral identical with $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$ or $5CaO \cdot 6SiO_2 \cdot 5H_2O$. Shrivastava and Glasser have reported ion exchange reactions of synthetic 1.1 nm tobermorite with Mg^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+} [5, 6]. The authors have investigated the $3Ca^{2+} \rightleftharpoons 2Fe^{3+}$ exchange reaction in 1.1 nm tobermorite at room temperature [7]. The aim of this communication is to present the data on $Ca^{2+} \rightleftharpoons Pb^{2+}$ exchange reaction of synthetic 1.1 nm tobermorite.

2. Experimental details

The ion exchanger, synthetic 1.1 nm tobermorite has been prepared by autoclaving pure CaO (prepared by igniting AR $CaCO_3$ at 1000° C) and micronized optical grade quartz (0.09% non-volatile with HF) in stainless steel autoclaves at 175° C under saturated steam pressure for 48 h. The detailed procedure described by Kalousek has been followed [8]. The product thus obtained was washed several times with decarbonated water and acetone and dried in carbon dioxide free air. This product when placed in water gives a pH ~ 8. On examination under electron microscope the synthetic product was found to be in the form of thin plate-like crystals of length 0.5 to 5.0 μm (Fig. 1). The X-ray diffraction pattern of this product matches well with standard pattern for 1.1 nm tobermorite as reported by Taylor *et al.* [9]. Eighteen reflections having *d* spacings between 1.13 to 0.1627 nm matched with the standard both in intensity and positions. The additional reflections have also been listed in Table II.

The typical ion exchange experiments have been carried out by vigorously shaking Pb^{2+} solutions (100 to 1800 p.p.m.) with 1 g of synthetic tobermorite in the nine sealed polythene bottles for 7 days. The details have already been described in earlier communications [5]. The ion exchange data have been generated from analysis of calcium and lead contents in the solution and solid phase after the steady state has been reached. The solid exchanged product has been analysed for lead after borate fusion [10, 11]. The lead content was determined complexometrically by EDTA titration. The calcium released as a result of exchange reaction has been estimated volumetrically by titrating against standard $KMnO_4$ solution after precipitation as calcium oxalate.

3. Results and discussion

Analyses of the lead exchanged tobermorite samples show that it is possible to prepare tobermorites having as much as ~ 10% of lead without any significant loss of crystallinity. The $Pb^{2+} \rightleftharpoons Ca^{2+}$ reaction in tobermorite can be summarized as follows

$$Pb^{2+}_{\text{solution}} + Ca^{2+}_{\text{tobermorite}} \rightleftharpoons Pb^{2+}_{\text{tobermorite}} + Ca^{2+}_{\text{solution}} \quad (1)$$

Fig. 2 shows ion exchange isotherm at 25° C. The thermodynamics of the exchange reaction can be worked out by the calculation of selectivity coefficient which is defined as

$$K_c = \frac{A_z B_s}{B_z A_s} \cdot \frac{\gamma_B}{\gamma_A} \quad (2)$$

where A_s and A_z represent the equivalent cation fractions of the ion A in solution and zeolitic solid phase, respectively. B_s and B_z represent the corresponding equivalent cation fractions of ion B and γ_A and γ_B are the respective activity coefficients in the aqueous

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TABLE I Ion exchange data for $Ca^{2+} \rightleftharpoons Pb^{2+}$ exchange in 1.1 nm tobermorite

Initial concentration of Pb^{2+} ($m\,mol\,dm^{-3}$)	Lead in solid phase		Lead in solution after equilibrium ($m\,mol\,dm^{-3}$)	K_d*	Calcium released $m\,mol\,g^{-1}$ of tobermorite	Mols Ca^{2+} released/mol Pb^{2+} in solid	Empirical formulae of lead exchanged products	At % Ca replacement
	wt %	Total m mols						
0.4826	0.93	0.0452	0.025	1797.101	0.0515	1.14	$Ca_{4.89}Pb_{0.033}Si_6O_{16}H_2 \cdot 4H_2O$	0.76
0.9652	1.84	0.0901	0.0531	1672.727	0.0917	1.02	$Ca_{4.86}Pb_{0.066}$	1.36
1.9304	3.64	0.1808	0.1168	1504.132	0.1989	1.10	$Ca_{4.78}Pb_{0.132}$	2.95
2.8956	5.35	0.2698	0.1921	1344.221	0.2824	1.05	$Ca_{4.72}Pb_{0.196}$	4.19
3.8610	6.96	0.3567	0.2664	1260.870	0.3012	0.84	$Ca_{4.71}Pb_{0.262}$	4.47
4.8260	8.55	0.4428	0.3996	1032.609	0.4548	1.03	$Ca_{4.60}Pb_{0.322}$	6.74
5.7912	9.99	0.5246	0.5492	877.856	0.5202	0.99	$Ca_{4.55}Pb_{0.384}$	7.71
7.2390	11.67	0.6212	0.9657	583.208	0.6390	1.03	$Ca_{4.46}Pb_{0.453}$	9.48
8.6868	13.08	0.7064	1.5984	394.928	0.6829	0.97	$Ca_{4.43}Pb_{0.514}$	10.13

*K_d is defined as the ratio of the amount of lead sorbed per gram of sample to the amount of unsorbed lead per ml solution.

phase. We make the assumption that in dilute solutions the activity coefficients approach unity. The plot of $\log_{10} K_c$ as a function of fractional atomic replacement of calcium from tobermorite is linear (Fig. 3). The free energy of the exchange reaction has been calculated from Fig. 4 following the method of Thomas and Gaines [12]. They used the following equation

$$\ln K = (b - a) + \int_0^1 \ln K_c \cdot dZ_M \qquad (3)$$

where b is the charge of the releasing ion in solution phase, a the charge of the entering ion in solid phase, K_c the selectivity coefficient and Z_M the equivalent fraction of the entering ion in solid phase. The K_d varies from 1797.10 (for 100 p.p.m. solution) to 394.93 (for 1800 p.p.m. solution). The free energy of the exchange reaction worked out is -209.9395 (cal equivalent)$^{-1}$.

Table I gives a summary of the mass balance obtained on the analysis of solution and solid phases. The molar ratio of calcium to lead varies from 0.84 to 1.14. The lead exchanged tobermorites can be assigned the following empirical formulae

$$Ca_{5-x}Pb_xSi_6 \ldots nH_2O$$

where x varies from 0.033 to 0.514. The release of equivalent amount of calcium from tobermorite further confirms that the incoming Pb^{2+} ions substitute Ca^{2+} ions in the structure. The first mechanism of ion exchange reaction in 1.1 nm tobermorite was given by Roy *et al.* to explain Cs^+ uptake [2]. Cs^+ ion exchange was said to be caused by Al^{3+} substitution, i.e. H_3O^+ subsequently participating in exchange with Cs^+. Our studies on a series of cations, however, have confirmed the release of Ca^{2+} ions in almost equivalent amounts. Since thermal data for cation exchanged tobermorites are almost similar to that of tobermorite, the theory that the exchange reaction taking place via H_3O^+ needs additional experimental evidence to that effect. The exchange reaction can be interpreted in the light of the structure suggested by Hamid *et al.* [13, 14]. All calcium atoms are not crystallochemically identical. The X-ray data of the exchanged products do not show significant expansion in the basal spacings. This

TABLE II X-ray powder diffraction data for lead exchanged tobermorite containing 8.55 wt % lead (Sample No. 6)

Sample SoNo	*d* spacings (nm)	I/I_{max} (%)	*h k l*	Sample SoNo	*d* spacings (nm)	I/I_{max} (%)	*h k l*
1	1.118 91	3	0 0 2	20	0.195 20	10	0 3 7
2	0.704 32	12	0 1 1	21	0.185 65	19	2, 1, 11
3	0.544 68	11	2 0 1	22	0.183 87	26	0 4 0
4	0.445 07	16	0 0 5	23	0.169 76	11	4 3 5
5	0.423 03	31	1 0 5	24	0.166 92	7	2 3 9
6	0.359 39	63	1 1 5	25	0.162 12	34	4, 1, 11
7	0.348 99	18	2 0 5	26	0.153 03	5	0 4 8
8	0.333 79	25	0 1 6	27	0.142 42	12	7 2 4
9	0.327 40	75	0 2 3	28	0.139 02	4	8 0 2
10	0.308 16	100	2 2 0	29	0.133 16	10	8 1 3
11	0.297 15	12	2 2 2	30	0.125 38	4	2 5 8
12	0.280 97	40	0 0 8	31	0.121 87	4	8 2 7
13	0.270 12	21	2 2 4	32	0.117 73	4	2 6 4
14	0.262 75	50	0 2 8	33	0.112 14	4	10, 1, 2
15	0.249 72	14	4 0 4				
16	0.241 29	3	0 2 7				
17	0.234 40	8	1 3 2				
18	0.222 50	13	3 0 8				
19	0.203 03	22	3 3 2				

Orthorhombic, Lattice constants: $A = 0.004618$, $a = 1.134\,89$ nm
$B = 0.01098$, $b = 0.736\,01$ nm
$C = 0.001183$, $c = 2.242\,28$ nm

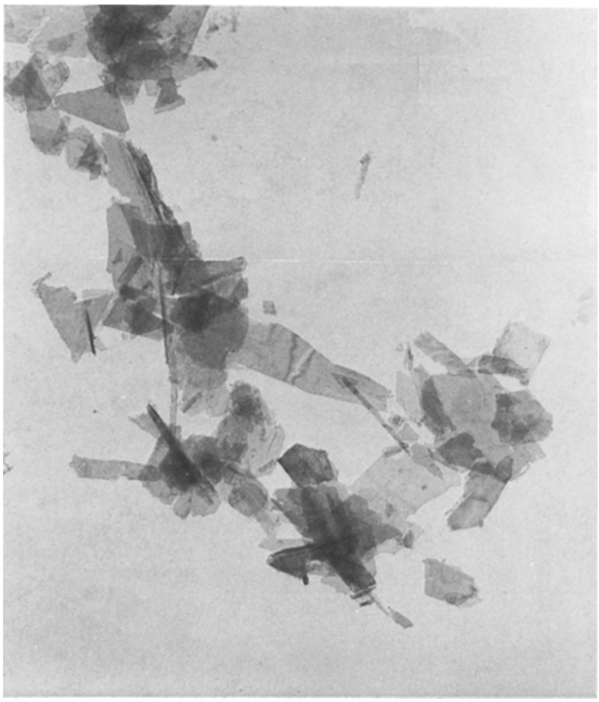

Figure 1 Electron microphotograph of 1.1 mm tobermorite.

suggests that the exchange reaction may be associated with simultaneous silicate polymerization, i.e. condensation of Si–O portion of the structure [5, 15, 16].

1.1 nm tobermorite is an important phase in the hydration reaction in Portland cements. Portland cements hydrated at 25° C contain C–S–H phase which is fairly amorphous. When silicious blending agents are added, the C–S–H phase may become tobermorite like as ageing progresses. It is interesting to note that while C–S–H in unmodified cements show little cation exchange, this capacity may be significantly enhanced on addition of blending agents. Studies on the properties of tobermorite may thus shed new light on the behaviour of hydrogel constituents of blended cements.

Further it is also notable that the crystallinity of the exchanger remains intact, therefore, it appears that tobermorite is a new potentially useful ion exchange material, stable in neutral and alkaline solution.

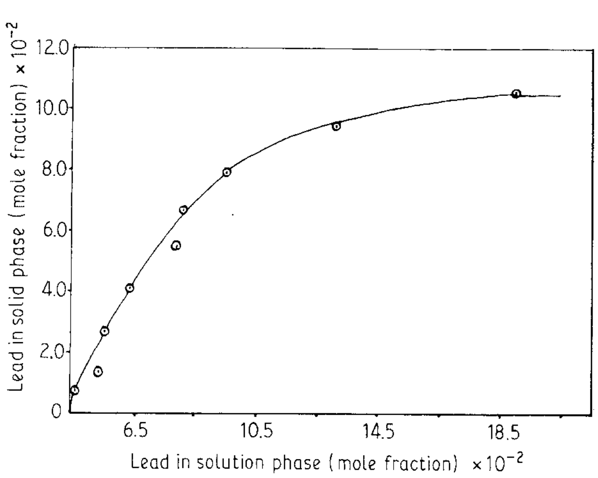

Figure 2 Ion exchange isotherm for $Pb^{2+} \rightleftharpoons Ca^{2+}$ system in 1.1 nm tobermorite.

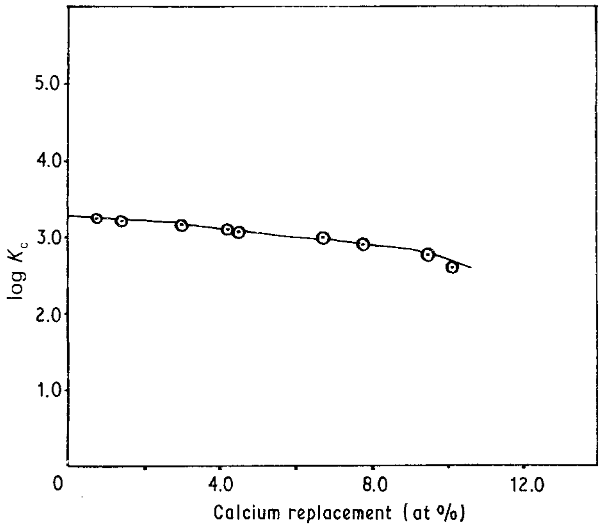

Figure 3 Fractional atomic replacement of calcium as a function of selectivity coefficient.

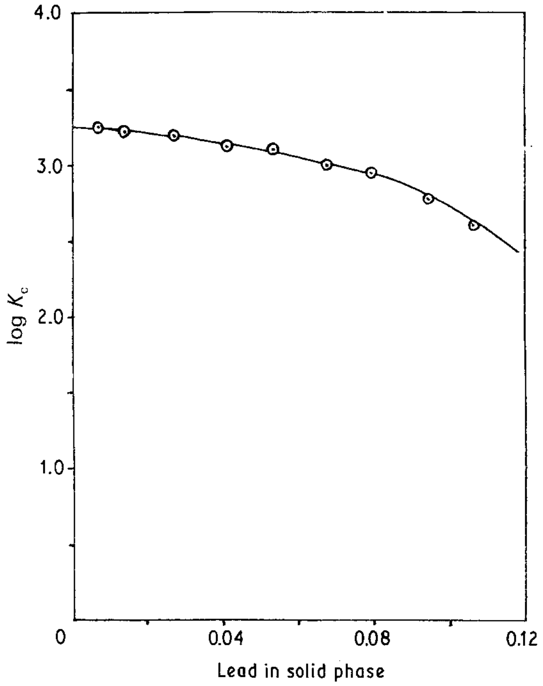

Figure 4 Selectivity coefficient as a function of equivalent fraction of lead in solid phase.

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