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Mössbauer Study on Iron-Exchanged Calcium Silicate Hydrate: $Ca_{5-x}Fe_xSi_6O_{18}H_2 \cdot nH_2O$

N. K. LABHASETWAR* AND O. P. SHRIVASTAVA
Department of Chemistry, Dr. H. S. Gour University, Sagar, India 470 003

AND Y. Y. MEDIKOV
Institute of Solid State Chemistry, Siberian Academy of Sciences,
Novosibirsk, 630091 U.S.S.R.

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Preliminary investigations on the calcium ⇌ iron ion-exchange reaction in the calcium silicate hydrate identical to 11-Å tobermorite have been reported by the authors. The thermodynamics of this exchange reaction has been developed with the help of analytical data of solid and solution phases. As a significant amount of iron could be introduced into 11-Å tobermorite, the Mössbauer spectroscopic studies have been performed on iron exchanged product. Mössbauer study shows that the Fe^{3+} ions are surrounded by the both distorted and undistorted oxygen octahedra. The ion-exchange phenomenon in this compound resembles that of zeolites and clays in some respects. The exchanger shows remarkable affinity toward iron in aqueous medium.

Introduction

The 11-Å tobermorite is a calcium silicate hydrate close to $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$. It is an important phase formed during the hydration reaction of portland cements (*1, 2*). This compound shows remarkable ion-exchange capacity toward iron (*3*) as well as a few other cations (*4–11*). The ion-exchange data for the calcium ⇌ iron reaction of 11-Å tobermorite is given in Table I along with some thermodynamic parameters. The details of this exchange experiment have been described elsewhere (*3*). The Fe^{3+} ions are supposed to take positions of the released Ca ions in 11 Å tobermorite framework. The crystallinity of the exchanger remains intact after cation exchange in dilute solutions which is confirmed by X-ray powder diffraction data of the exchanged products. Since an appreciable amount of iron could be introduced in the exchanger's framework, it was thought worthwhile to perform Mössbauer studies on iron-exchanged 11-Å tobermorite. In this communication we report the study of positions and steric pecularities of the introduced iron in the tobermorite framework, using Mössbauer data.

Experimental

The exchanger 11-Å tobermorite was synthesized by the method described by Kalousek (*6*). Characterization and examination of the synthesized product has been done by chemical analysis, X-ray powder

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* To whom correspondence should be addressed.

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TABLE I

ION-EXCHANGE DATA FOR $2Fe^{3+} \rightleftharpoons 3Ca^{2+}$ EXCHANGE IN SYNTHETIC 11-Å TOBERMORITE

Initial concentration of Fe^{3+} in solution		Iron in solid phase		Iron in solution after equilibrium	Distribution coeff.	Calcium released from tobermorite	Ca^{2+} released/ Fe^{3+} in solid	Empirical formulae of iron-exchanged derivatives
(ppm)	(mmol dm^{-3})	(wt%)	(mmol g^{-1})	(mmol dm^{-3})	$K_d{}^a$	(mmol g^{-1})	(mmol)	
100	1.790	0.930	0.166	0.090	1860.0	0.242	1.46	$Ca_{4.82}Fe_{0.12}Si_6O_{18}H_2 \cdot 4H_2O$
200	3.580	1.820	0.326	0.181	1802.0	0.463	1.42	$Ca_{4.66}Fe_{0.24}$ ·····
400	7.160	3.620	0.648	0.460	1408.5	0.939	1.45	$Ca_{4.31}Fe_{0.47}$ ·····
600	10.74	5.410	0.969	0.760	1276.0	1.366	1.41	$Ca_{4.00}Fe_{0.71}$ ·····
800[b]	14.32	7.250	1.298	1.180	1100.0	1.804	1.39	$Ca_{3.68}Fe_{0.95}$ ·····
1000	17.90	8.990	1.609	1.799	894.50	2.301	1.43	$Ca_{3.32}Fe_{1.18}$ ·····
1200	21.48	10.45	1.871	2.740	683.00	2.619	1.40	$Ca_{3.09}Fe_{1.37}$ ·····
1500	26.85	12.51	2.240	4.240	527.80	3.136	1.40	$Ca_{2.71}Fe_{1.64}$ ·····
1800	32.23	14.12	2.528	6.610	382.60	3.412	1.35	$Ca_{2.51}Fe_{1.85}$ ·····
2000	35.81	14.82	2.654	9.275	286.10	3.556	1.34	$Ca_{2.40}Fe_{1.94}$ ·····
2500	44.76	15.26	2.733	17.44	156.67	3.607	1.32	$Ca_{2.36}Fe_{1.20}$ ·····
3000	53.72	15.47	2.770	25.96	106.69	3.629	1.31	$Ca_{2.35}Fe_{2.02}$ ·····
5000	89.53	16.20	2.901	60.52	47.930	3.771	1.30	$Ca_{2.24}Fe_{2.12}$ ·····

[a] K_d is defined as the ratio of the amount of iron sorbed per gram of sample to the amount of unsorbed iron per milliliter solution.

[b] Sample used for Mössbauer studies.

diffraction (*12*) (Table II) and electron microscopy. The ion-exchange reactions were typically carried out by shaking 1-g synthetic tobermorite sample with 100 ml of ferric-nitrate solutions containing 100–5000 ppm Fe^{3+} separately in each of 13 sealed polythene bottles for 7 days. On reaching the steady state both solid and solution phases were analyzed for iron and calcium after filtration and thorough washing with double-distilled water. The amount of iron in the solid phase has been determined complexometrically after borate fusion (*13, 14*). Calcium has been estimated volumetrically by titrating against standard $KMn0_4$ solution after precipitation as calcium oxalate (*15*). The analytical data has been summarized in Table I. Other experimental details have been described in our earlier communication (*3*). To check the crystallinity of the exchanger after ion exchange, the XRD analysis of the exchanged product has been performed (Table II). These data show that the crystallinity of the exchanger remains intact after ion exchange. Thermal analysis of the exchanged product has been carried out to study the involvement of water molecules in exchange reactions. Mössbauer study on iron-exchanged tobermorite have been carried out on a γ-JRS-4M Mössbauer spectrometer (Russian) working in a constant acceleration regime with moving sample and stationary source. The time of exposure was 24 hr. Isomeric shift (δ) were determined relatively to α-Fe. The Mössbauer spectrum has been treated by least square fitting on computer. The Mössbauer study has been carried out on the sample derived from set 5, which has been prepared by equilibriating 1 g of 11-Å tobermorite with ferric-nitrate solution containing 14.32 m mol/dm³ (800 ppm) of Fe^{3+} ions at room temperature.

Results and Discussion

It is now well established that 11-Å tobermorite can act as an ion exchanger for sev-

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR TOBERMORITE AND IRON-EXCHANGED TOBERMORITE[a]

11-Å tobermorite		Iron-exchanged tobermorite		
d-spacings (Å)	I/I_{max} (%)	*d*-spacings (Å)	I/I_{max} (%)	*hkl*
11.21	9.18	11.13	4.00	002
7.02	3.88	7.02	20.25	011
5.48	19.31	5.44	14.54	201
4.25	4.29	4.23	74.39	105
3.63	14.35	3.63	26.91	115
3.51	11.79	3.50	16.00	205
3.32	8.58	3.33	31.64	016
Absent		3.23	30.25	007
3.08	100.00	3.08	100.00	220
Absent		3.03	38.29	313
2.97	37.35	2.97	13.14	222
2.81	45.80	2.80	60.06	400
2.70	6.38	2.70	11.82	224
2.34	8.58	2.34	12.69	132
Absent		2.28	14.54	209
2.24	14.35	2.24	14.06	308
2.14	8.88	2.14	9.38	423
2.06	10.12	Absent		513
2.02	17.15	2.02	30.25	332
1.99	8.29	Absent		319
1.95	4.94	1.95	14.06	037
1.84	29.75	1.83	27.56	040
1.81	11.11	Absent		0,1,12
1.72	8.00	1.68	44.72	435
1.67	11.79	1.66	10.56	293
1.61	2.61	1.60	4.00	4,1,11
1.54	6.63	1.52	6.89	048
Absent		1.50	23.16	2,2,13

[a] Sample containing 15.47 wt% iron. Orthorhombic, Lattice constants: $A = 0.004618$, $a = 11.34$ Å, $B = 0.010980$, $b = 7.36$ Å, $C = 0.001183$, $c = 22.42$ Å.

eral cations. It shows a remarkable ion-exchange capacity which is comparable with that of zeolites and clay minerals for many of them. The cation uptake in the calcium silicate hydrate framework arises as a result of (a) broken bonds from edges, (b) outer planar surfaces of crystals, (c) interlayer inclusion of cations to make up the charge balance, or (d) reaction with the structural calcium. It is not necessary that all these factors operate in all exchange reactions but at least one of them is essential for the uptake of the cations. We have noted high uptake of Fe^{3+} in 11-Å tobermorite. As much as ~16 wt% iron could be loaded on the exchanger's framework. On the basis of analytical data this exchange reaction of 11-Å tobermorite can be represented by the equilibrium

$$2\,Fe^{3+}_{solution} + 3\,Ca^{2+}_{tobermorite} \rightleftharpoons 2\,Fe^{3+}_{tobermorite} + 3\,Ca^{2+}_{solution} \quad (1)$$

The ion-exchange isotherm of this reaction

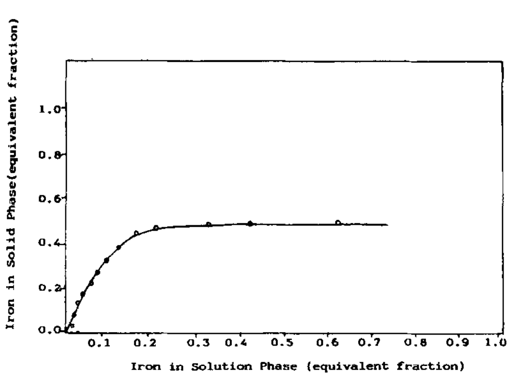

FIG. 1. Ion-exchange isotherm for $2Fe^{3+} \rightleftharpoons 3Ca^{2+}$ exchange in 11-Å tobermorite.

is shown in Fig. 1. The average value of free energy for this reaction is $\Delta F_{298} = -498 \pm 15$ cal/eq. The free energy calculations have been done on the basis of modified method of Gaines and Thomas (*16*) as described by Sherry and Walton (*17*). This negative value of free energy indicates affinity of the exchanger toward Fe^{3+} cations. The mass balance data also reveal that the calcium : iron molar ratio is about 1.5 : 1, which agrees with the expected value of molar ratio Ca/Fe for the exchange reaction represented by Eq. (1). The mechanism of the ion-exchange reaction in 11-Å tobermorite was first proposed by Roy *et al.* (*4, 5*) and Kalousek (*6*). The mechanism of Cs^+ uptake was explained by Al^{3+} substitution for Si^{4+}, i.e., H_3O^+ subsequently participating in exchange with Cs^+. Kalousek pointed out that in order to maintain electrical neutrality the possible substitutions are (Al^{3+} + H^+) for Si^{4+} or $2Al^{3+}$ for (Si^{4+} + Ca^{2+}) or $4Al^{3+}$ for $3Si^{4+}$. Unsubstituted 11-Å tobermorite also exhibits cation exchange although it does not contain aluminum. The thermal data remain practically unchanged after exchange, indicating that water does not take part in this exchange process. Our investigations on a series of cations (*3, 7–11*) have, however, confirmed the release of Ca^{2+} ions in almost equivalent amounts to balance the charge. The mechanism of the exchange reaction in 11-Å tobermorite can be best interpreted in light of the structure suggested by Hamid (*18*). The tobermorite structure has infinite Si_3-$(O/OH)_9$ chains running parallel to the *b* axis which are linked together by calcium atoms. Each calcium atom is coordinated with seven oxygen atoms. In general Ca(1), Ca(2), Ca(3), and Ca(4) are coordinated with four planar oxygen atoms, two oxygens above or below, and the seventh oxygen forming a tetragonal pyramid (Fig. 2). The octahedral coordination of the fifth calcium is very much distorted. It is expected that the interlayer calcium content is responsible for charge balance in cation-

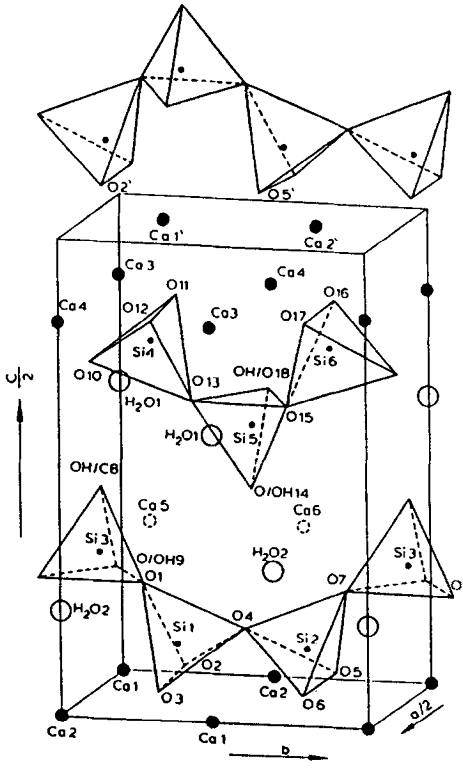

FIG. 2. A three-dimensional view of the tobermorite structure using the orthorhombic axis $a/2$ = 5.58 Å, b = 7.39 Å, and $c/2$ = 11.389 Å. The dotted Ca atoms are statistically distributed. (after S.A. Hamid, Ref. (*16*)).

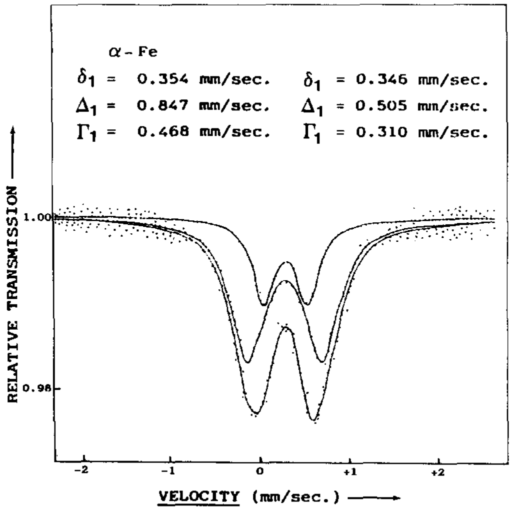

FIG. 3. Mössbauer spectrum of iron-exchanged tobermorite.

exchange reactions of 11-Å tobermorite. The most probable and expected sites for introduced Fe^{3+} ions are the interlayer spaces vacated by releasing Ca atoms. To study the geometric positions and surroundings of Fe ions we have tried to interpret the Mössbauer spectrum of iron-exchanged tobermorite. As seen from Fig. 3 the plot of the Mössbauer spectrum consists of one doublet with isomeric shift (δ) = 0.35 ± 0.02 mm/sec and quadrupole splitting Δ = 0.72 ± 0.02 mm/sec. Such a value for δ is typical for Fe^{3+} in a high spin state in an octahedral surrounding of oxygen but the large value of Δ and the line widths Γ = 0.468 ± 0.02 mm/sec show that oxygen octahedra are neither ideal nor similar over the bulk. To estimate the content of nondistorted octahedra of oxygen surrounding the Fe^{3+} cations, the Mössbauer spectrum has been treated by computer as the superposition of two doublets. After resolving the spectrum, it has been observed that the doublet with relative intensity of 29 ± 5% and δ = 0.36 ± 0.02 mm/sec may be attributed to Fe^{3+} cations placed in nondistorted octahedra because the line width is small (Γ = 0.31 ± 0.02 mm/sec) and the quadrupole splitting, Δ = 0.50 ± 0.02 mm/sec, is also not high. The second doublet with relative intensity of 71 ± 5% has practically the same isomeric shift δ = 0.35 ± 0.02 mm/sec but the quadrupole splitting Δ = 0.85 ± 0.02 mm/sec and Γ = 0.47 ± 0.02 mm/sec are considerably more than that of the first one. This doublet can be attributed to Fe^{3+} surrounded by distorted oxygen octahedra. In this way, Mössbauer study provided valuable information particularly about surroundings of Fe^{3+} cations. With the help of these data, it may be concluded that the introduced Fe^{3+} takes the position of released Ca^{2+} ions. The iron present in place of the fifth calcium atoms is expected to be present in the distorted octahedral surrounding of oxygen atoms, while the rest of the iron might be present in place of Ca(4) or other Ca sites. The regular tetragonal pyramidal surrounding of these Ca atoms is expected to be changed in regular octahedra in the case of Fe^{3+} due to comparatively greater attraction of iron with oxygen. The thermogravimetric curve of iron-exchanged tobermorite (Fig. 4) shows a break between 660 and 740°C, although the total water loss is almost the same for both compounds (11-Å tobermorite and iron-exchanged tobermorite). Farmer *et al.*

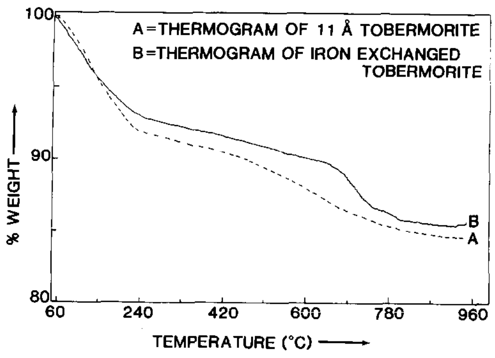

FIG. 4. Thermogram of 11-Å tobermorite and iron-exchanged tobermorite.

(*19*) suggested that water loss above 400°C is due to elimination of hydroxyl groups. In the case of iron-exchanged tobermorite the break at higher temperature in the thermogram could be due to firm attachment of OH^- groups with Fe^{3+} cations rather than Ca^{2+}.

Thus, there are reasons to suggest that Ca^{2+}, the releasing ion, is responsible for the cation-exchange activity of 11-Å tobermorite. It is possible that the Fe^{3+} cations can enter into the structure of tobermorite and take positions of released Ca^{2+} without much loss of crystallinity. It is interesting that the exchange properties of 11-Å tobermorite do not depend solely on counterions as Ca should be considered a compositional element. In this respect, 11-Å tobermorite belongs to a new category of silicate ion exchangers.

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