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Divalent ion uptake of heavy metal cations by (aluminum + alkali metals) – substituted synthetic 1.1 nm-tobermorites

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The reactions of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} or Hg^{2+} synthetic (Al + alkali metal) – substituted tobermorites were studied. Among these cations, Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, pb^{2+} and Hg^{2+} appears to exchange with outer planar surface of Ca^{2+} of tobermorites due to the break down of structural Ca-O bonds, in addition to the substituted alkali metals in the structure. But it is difficult to delineate the extent of this reaction from the precipitation of the concerned ions as carbonates, hydroxy carbonates, hydroxy nitrates or hydroxides. The uptake of metal ions by these solids led to their amorphization in many cases due to the partial exchange and the acidic nature of metal solutions, and hence their reactions are not strictly analogous to cation exchange in zeolites and clays. The order of ion uptake has been found in the following order: $Fe^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+} > Mn^{2+} > Hg^{2+} > Cd^{2+} > pb^{2+}$. *© 2001 Kluwer Academic Publishers*

1. Introduction

The tobermorite group of hydrated calcium silicates includes a variety of phases with different crystallinity and variations in chemical composition. Of these, tobermorite [$Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$] is referred to as 1.13 nm-tobermorite based on the thickness of the elementary layers in its structure. The crystal structure of 1.13 mn-tobermorite was first investigated by Megaw and Kelsey [1] and subsequently by Hamid [2]. It's structure is also similar to that in 2 : 1 clay minerals [3] and its basic layer consists of a central sheet of CaO_2 which is sandwiched by rows of $SiO_2(OH)_2$ tetrahedra that are linked into chain running parallel to the b-axis direction. The presence of ≡Si-O-Si≡ bridges between the chains has been proposed by several authors [4, 5] and unambiguously confirmed by ^{29}Si MASNMR Spectroscopy [6, 7].

The presence of Al^{3+} -and/or alkali ions is known to be among the most influential factors with regard to tobermorite formation and its final silicate anion structure [8]. Tobermorites substituted with [$Al^{3+} + Na^+$] for Si^{4+} have been discovered [9–11] to show cation exchange and selectivity for some catoins. The Al^{3+} is isomorphously substituted for Si^{4+} in tetrahedral sites and alkali metal ions such as Na^+ are situated in the interlayer [12] and compensate the deficient charge. The substituted tobermorites constitute a new family of inorganic ion exchangers and are characterized by their high selectivity for Cs cations [10], the Cs^+ selectively exchanging with Na^+ ions which are located in the interlayer position [12].

It was found [13] that tobermorites synthesized from $Ca(OH)_2$ and fly ash waste materials exhibit Cs and Sr selectivity than those synthesized from Ca(OH) and SiO_2 under the same conditions. This is due to more extensive Al^{3+} incorporation with fly ash. In a similar way, it was reported [14] that Al-substituted tobermorite as an additive to OPC was found to fix about 77% of Sr^{2+} in cement matrix against 17% fixation in the OPC.

The objective of this research was to determine the exchange property of (aluminum + alkali metals)-substituted synthetic 1.1 nm-tobermorires toward some 3d-transition metals and toxic cations from the viewpoint of cation separation (purification) chemistry. This study was undertaken in order to fully realize potentialities of these exchangers in the above research filed and especially in hazardous waste stream and nuclear waste disposal areas.

2. Experimental and methods

2.1. Preparation of (Al^{3+} + alkali metals) – substituted tobermorites

Tobermorites of different chemical composition were prepared by mixing stoichiometric amounts of CaO and

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SiO_2 (below 10 μ). 15 mol% of SiO_2 was replaced by Al $(OH)_3$ and the mixed powder was added to 20 fold of its weight of either deionized water or 1 M solution of NaOH, KOH or 0.5 solution of LiOH, and stirred for 30 minutes in a 250 ml beaker. The contents of the beaker were transferred to teflon coated stainless steal autoclave bombs and heating the bombs at 180°C for 20 h. Hydrothermal treatment of sodium meta-silicate and $AlCl_3$. $6H_2O$ was also used instead of NaOH or $Al(OH)_3$ for 96 h in some runs. After the autoclaves were cooled, the reaction products were mixed in the autoclaves and then centrifuged to separate the solid and solution phases. The solids were washed with deionized water to remove soluble components. The solids products were dried at 90°C for 3 h and then subjected for chemical analysis and powder X-ray diffraction (XRD) analysis using an x-ray diffractometer with Ni-filtered Cu Kα radiation.

2.2. Total cation-exchange-capacity (CEC) determination

The CEC was determined by suing the method reported previously [15]. The procedure can be briefly describe as follows: A portion of tobermorite (50 mg) was washed twice (equilibration time was 30 min. for each washing) with KCl to saturate all the exchange sites with K^+, followed by five washings with 10^{-2} N KCl to remove the excess of KCl to prevent hydrolysis. The K^+ ions from the exchange sites were displaced by four washings (30 min. equilibration time per washing) with 0.2 N CsCl. The solution was collected and analyzed for K^+ by AES and the total CEC was determined.

2.3. Cation reaction experiments

The divalent metal cations reactions were conducted following the standard procedure reported in [16]. 10 mg of each solid was equilibrated for different periods in glass vials with 5 ml nitrate, sulphate or chloride solution of 100, 200, 500 or 1000 mg/L of Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, pb^{2+}, Cd^{2+} or Hg^{2+}. Nitrate anions were used for pb^{2+}, Cu^{2+} and Hg^{2+}, sulphate anions for Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+} and Fe^{2+} and chloride anions for Cd^{2+}. After different periods of equilibration the solutions and the solid phases in the glass vials were separated by centrifugation and a part of the supernatant solution was collected for chemical analysis using atomic absorption spectroscopy (AAS). The pH of the equilibrium solution for some reactions in the glass vials was immediately measured.

The changes in the crystal structure of some solid phases upon the reaction was also followed by X-ray diffraction and IR-spectroscopy techniques.

3. Results and discussion

Table I Shows the chemical composition and the cation exchange capacity of (aluminum + alkali metal)-substituted tobermorites, while the change in pH-value upon the reaction are given in Table II.

Results of CEC show that (Al + alkali metals) substituted tobermorites reveal higher values than the unsubstituted one by about 4-5 times. They also possess approximate by the same CEC values, except in case of (Al + Na) substituted-tobermorite prepared from sodium meta-silicate and $AlCl_3{\cdot}6H_2O$ (Table I). The higher CEC in (Al + K) tobermorite compared to the corresponding (Al + Na) and/or (Al + Li) samples prepared at the same condition may be attributed to the fact that K^+ is less hydrated than Na^+ or Li^+, and hence it can be easily substituted.

The pH-values of the initial cation metal solutions increased on reaction with the solids and also with increasing the reaction time. This could be attributed to the release of Ca^{2+} and/or alkali metal ions from the lattice structure of the solid in solution to from hydrated calcium or alkali metal ions during the course of reaction.

Results of the reaction of nine heavy metals with Ca^{2+} and/or alkali metals in tobermorite samples are presented in Figs 1–5 and Tables III–VII. In these reactions the exchange of $Ca^{2+} \Leftrightarrow M^{2+}$ in most cases seem to be non-stoichiometric (the reason will be discussed latter). But, generally the metal ions taken up by substituted solids are higher than in unsubstituted one as a function of time Figs 1–5 or concentration functions Tables III–VII. In this respect, Fe^{2+}, Co^{2+} and Ni^{2+} metal ion uptake by the solids were found to be higher than the other metals. Higher meq of these ions were taken up compared to the amounts of meq of Ca^{2+} released. The exchange reaction in substituted tobermorite was postulated [11, 17, 18] to take place from edge and planar surface sites and apparently from the interlayer Ca^{2+} sites, since tobermorite has the octahedral Ca (5) and Ca (6) which are very distorted

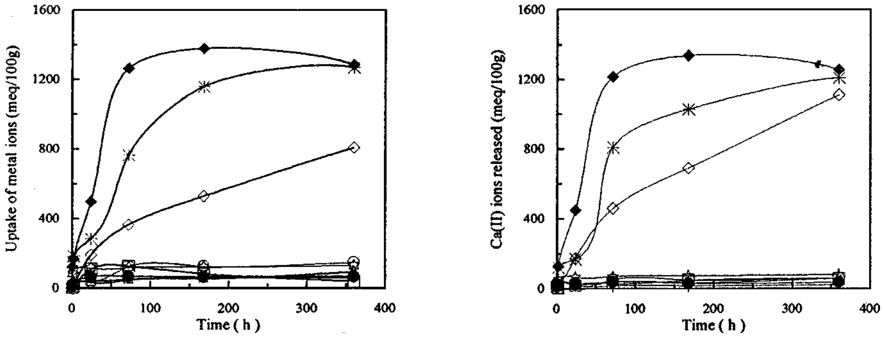
TABLE II Change in pH-values of initial metal ion solution (1000 ppm) due to the exchange reaction with some solids

Solid phase	Metal ion solution	pH of solution	pH after the reaction at: 2 h	360 h
(Al + Na) sub.-Tobermorite	Ni	6.67	7.55	8.36
	Fe	2.87	4.33	5.19
	Zn	2.71	6.48	6.76
	Hg	3.59	7.74	8.64
(Al + Li) sub.-Tobermorite	Co	6.56	7.75	8.65
	Mn	4.33	7.61	7.83

TABLE I Chemical composition and cation exchange capacity (CEC) of the synthesized solids

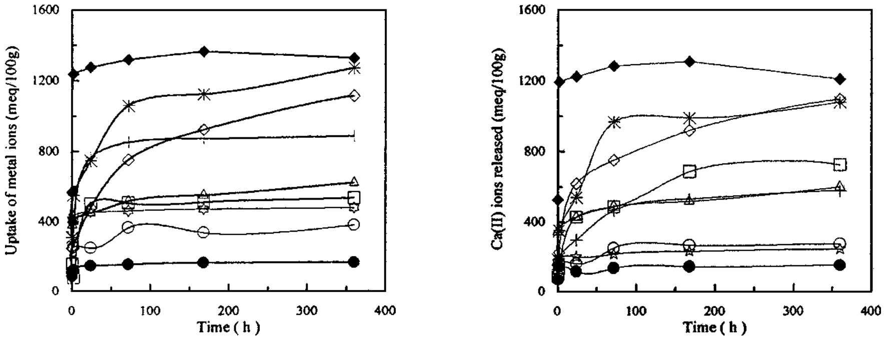
Solid phase	Chemical composition	CEC meq/100 gm
Unsubstituted-tobermorite*	$Ca_5Si_{5.2}O_{14.5}(OH)_2(3.5)H_2O$	35.5
15 mol% (Al + Li) sub.-tobermorite**	$Ca_5Li_{0.95}Al_{0.95}Si_{5.27}O_{16.09}(OH)_2 3.7H_2O$	141.8
15 mol% (Al + K.) sub.-tobermorite**	$Ca_5K_{0.9}Al_{0.9}Si_{5.1}O_{16}(OH)_2.\ 4.5H_2O$	151.9
15 mol% (Al + Na) sub.-tobermorite**	$Ca_5Na_{0.9}Al_{0.9}Si_{5.1}O_{16}(OH)_2\ 4.06H_2O$	140.4
15 mol% (Al + Na) sub.-tobermorite***	$Ca_5Na_{0.6}Al_{0.6}Si_{5.4}O_{16}(OH)_2.\ 5.02H_2O$	179.9

*Prepared for 168 h. **Prepared for 20 h. ***Prepared from solid. meta-silicate and $AlCl_3$-$6H_2O$ for 96 h.



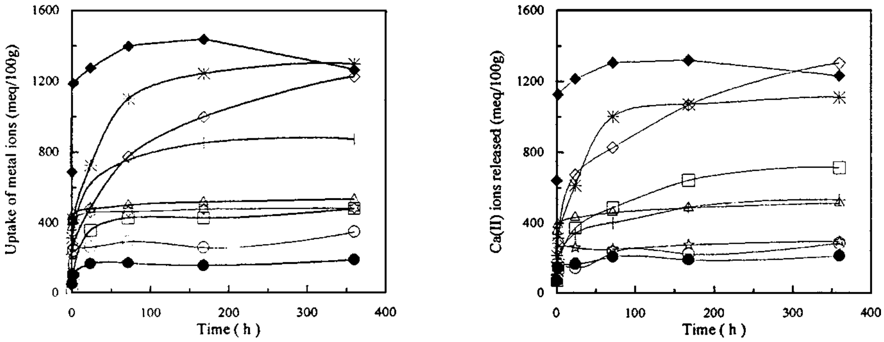
(A) (B)

Figure 1 (A) Uptake of metal ions from 1000 ppm aqueous solution by unsub.-tobermorite, (B) Amount of Ca ions released from unsub.-tobermorite.



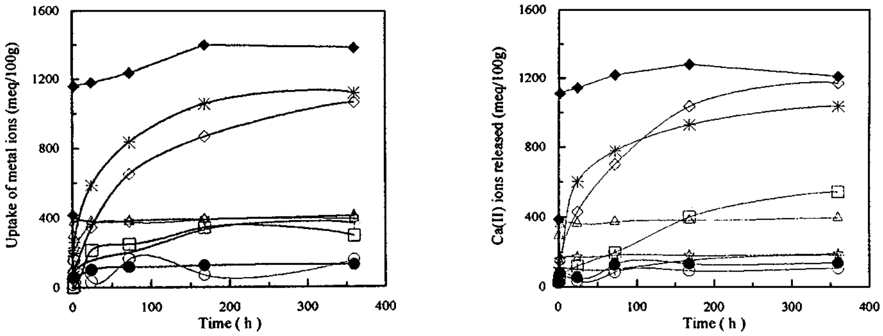
(A) (B)

Figure 2 (A) Uptake of metal ions from 1000 ppm aqueous solution by 15% (Al + Li) substituted tobermorite, (B) Amount of Ca ions released from 15% (Al + Li) substituted tobermorite.



(A) (B)

Figure 3 (A) Uptake of metal ions from 1000 ppm aqueous solution by 15% (Al + Na) substituted tobermorite, (B) Amount of Ca ions released from 15% (Al + Na) substituted tobermorite.



(A) (B)

Figure 4 (A) Uptake of metal ions from 1000 ppm aqueous solution by 15% (Al + K) substituted tobermorite, (B) Amount of Ca ions released from 15% (Al + K) substituted tobermorite.

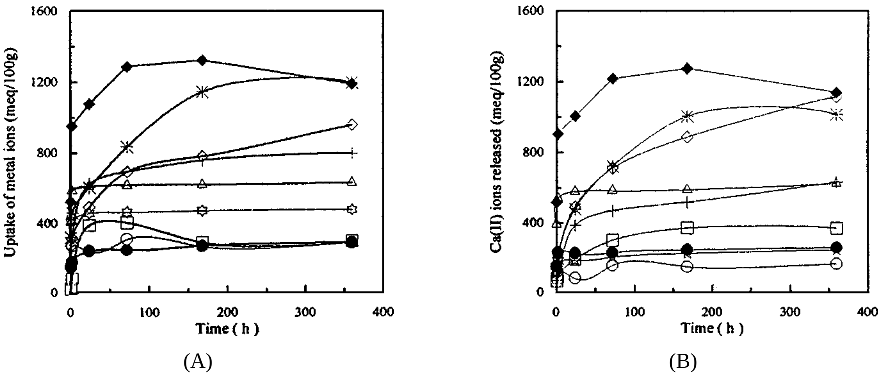


Figure 5 (A)Uptake of metal ions from 1000 ppm aqueous solution by 15% (Al + Na) substituted tobermorite, (B) Amount of Ca ions released from 15% (Al + Na) substituted tobermorite. (Prepared from Sod. meta silicate and $AlCl_3.6H_2O$) Ion metal □ Mn; ◆ Fe; ◇ Co; ✳ Ni; + Cu; △ Zn; ● Pb; ○ Cd; ✡ Hg.

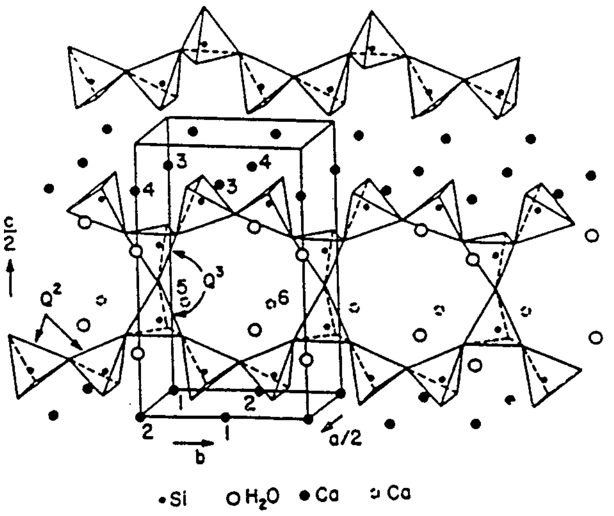


Figure 6 A three-dimensional view of anomalous 1.13 nm-tobermorite with Ca/Si = 0.83 molar ratio based on Hamids's$^{(2)}$ and ^{27}Al and ^{29}Si MASNMR data presented by Komarneni *et al.* [23] (The dotted circles indicate structural Ca^{2+} ions).

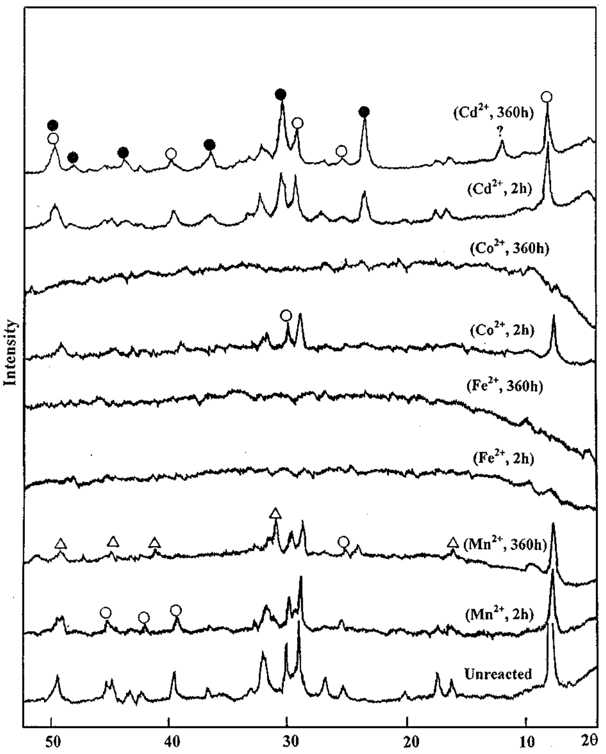


Figure 7 X-ray diffractograms of (Li + Al) Substituted-tobermorite reacted with 1000 ppm of Mn^{2+}, Fe^{2+}, Co^{2+} and Cd^{2+} solution for 2 and 360 hrs. (○ = Tobermorite, ● = Otavite ($CdCO_3$), △ = Rhodochrosite ($MnCO_3$).

and the Ca-O interaction is weak Fig. (6). Hence, they are expected to be exchangeable. On the other hand, the exchange of these ions are inhibited by their lager hydrated radii, so that it has a low CEC value. The measured value of CEC for unsubstituted-tobermorite in the present results agreed with the published data in literature [18, 19]. But in case of (Al + alkali) substituted-tobermorites the higher CEC values are due to the presence of alkali metals in additional to Al^{3+}. These values are located in the range between the CEC of clays and zeolites [20].

The exchange in this case appears to be a two steps process, first the alkali ion (Li^+, Na^+ or K^+) are rapidly exchanged and then the Ca^{2+} ions are exchanged, i.e. the available exchange sites increase and hence (Al + alkali) substituted-tobermorites, achieved higher CEC compared to the unsubstituted. Also, it was reported [12] that, the ≡Si-O-Si≡ bridges between layers present in substituted tobermorites, stabilize the structure and create zeolite-like cavities formed by eight (Si + Al) atoms (Fig. 6). It is difficult to draw a clear sharp picture about the real mechanism of this exchange reaction between the solids and the metal ions, due to the precipitation of the ions such as: Fe^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, pb^{2+} and Hg^{2+} as hydroxides, hydroxy carbonates or carbonate (as detect by XRD, Figs 7–9) during the reaction. The contents of these phases have been found to increase with increasing time of reaction and/or their initial concentrations. On the other hand, the reaction of Co^{2+} or Ni^{2+} did not lead to the formation of either hydroxides, hydroxy carbonates or even carbonates as cleared from XRD data; but a coloured precipitates on the surface of tobermorite solids was noted and their solutions became approximately colorless. This means that these precipitates may be in amorphous state and therefore they can not detected by XRD.

The reaction of Fe^{2+} led to a loss of crystallinity of the solids completely, even after 2 h of reaction, while in case of Ni^{2+}, Co^{2+}, or Cu^{2+}, the crystallinity was partially lost at the same time of reaction and completely

TABLE III Mass balance data of M^{2+} taken up by unsubstituted tobermorite and the released Ca^{2+} in solution after 2 h (reaction time)

Metal ion (M^{2+})	Initial concentration of M^{2+} (ppm)																			
	100					200					500					**1000**				
	M^{2+} uptake (meq/100mg)	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**
Mn	2.60	4.20	1.43	0.31	0.62	20.1	9.90	5.52	0.72	0.62	16.3	7.5	1.79	0.55	2.17	13.50	7.0	0.74	0.51	1.93
Fe	51.2	35.5	28.27	2.58	1.44	84.5	63.2	23.57	4.60	1.33	114.3	419.3	12.57	30.53	0.27	169.7	129.7	9.47	9.44	1.31
Co	12	2.0	7.07	0.14	6.0	33	13	9.22	0.95	2.54	26	18	3.06	1.30	1.44	24	22	1.41	1.60	1.09
Ni	120.8	118	70.91	8.59	1.02	76.3	90	22.39	6.55	0.85	125	127	14.68	9.25	0.98	186	123	10.92	8.95	1.51
Cu	18	19	11.43	1.38	0.95	17	18	5.40	1.31	0.94	19	19.9	2.41	1.45	0.95	23	21	1.46	1.53	1.09
Zn	28	13	18.31	0.95	2.15	35	15	11.45	1.09	2.33	39	15	4.58	1.09	2.60	35	21	2.29	1.53	1.67
Pb	16	13	33.16	0.95	1.23	16	14	16.58	1.02	1.14	26	19	10.77	1.38	1.36	28	23	5.80	1.67	1.22
Cd	8	14.6	8.99	1.06	0.55	13	19	7.31	1.38	0.68	16	29	3.59	2.11	0.55	22	38	2.47	2.77	0.58
Hg	6.4	19	12.85	1.38	1.34	10.9	21	10.94	1.53	0.52	102	47.7	40.98	3.47	2.14	105	57.2	21.09	4.16	1.84

TABLE IV Mass balance data of M^{2+} taken up by (Al+Li) substituted tobermorite and the released Ca^{2+} solution after 2 h (reaction time)

Metal ion (M^{2+})	Initial concentration of M^{2+} (ppm)																			
	100					200					500					**1000**				
	M^{2+} uptake (meq/100mg)	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**
Mn	178	83	97.7	6.30	2.15	196	125	53.8	9.5	1.57	168	144	18.45	10.9	1.17	80.0	132	4.39	10.03	0.61
Fe	112.3	102.1	62.66	7.76	1.09	251.2	205	70.08	15.58	1.22	531.6	622	59.32	47.28	0.85	1236	1192	68.97	90.60	1.03
Co	168	53	98.95	4.03	3.16	325	154	95.71	11.71	2.11	215	177	25.33	13.45	1.21	263	224	15.49	17.03	1.17
Ni	168	88	98.62	6.69	1.91	222	210	65.16	15.96	1.06	246	230	28.88	17.48	1.07	551	350	32.43	26.60	1.57
Cu	157	65	99.69	4.94	4.42	204	89	64.77	6.76	2.29	203	95	25.78	7.22	2.13	343	189	21.78	14.37	1.81
Zn	145	84	94.43	6.38	1.73	219	143	71.61	10.87	1.53	290	271	37.93	20.29	1.07	403	356	26.36	27.06	1.13
Pb	46	52	95.31	3.95	0.88	90	89	93.24	6.76	1.01	101	113	41.58	8.59	0.89	121	144	25.07	10.94	0.84
Cd	87	36	97.79	2.74	2.42	137	105	76.99	7.98	1.30	197	127	44.28	9.65	1.55	255	167	28.66	12.96	1.53
Hg	5.20	3.60	10.45	0.27	1.44	10.5	7.5	10.54	0.57	1.40	72.5	66.3	29.13	5.04	1.09	428	194.2	85.98	14.77	2.20

TABLE V Mass balance data of M^{2+} taken up by (Al+Na) substituted tobermorite and the released Ca^{2+} solution after 2 h (reaction time)

Metal ion (M^{2+})	Initial concentration of M^{2+} (ppm)																			
	100					200					500					**1000**				
	M^{2+} uptake (meq/100mg)	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**	**M^{2+} uptake (meq/100mg)**	**Ca^{2+} release (meq/100mg)**	**Wt. % of M^{2+} uptaken**	**% of Ca^{2+} released**	**M/Ca Molar ratio**
Mn	165	113	90.58	8.49	1.46	182	126	49.96	12.18	1.12	137	145	15.04	10.90	0.95	110.0	145	6.04	10.90	0.76
Fe	98.5	92.3	54.96	6.94	1.06	213	201	59.42	15.11	1.05	604.2	578	76.43	43.4	1.05	1187	1126	66.23	84.6	1.05
Co	161.7	79	95.24	5.94	2.05	322	198	94.83	14.89	1.63	278	245	32.75	18.42	1.13	263	300	15.49	22.56	0.88
Ni	169	36	99.2	2.71	4.69	285	223	83.65	16.76	1.28	304	248	35.68	18.65	1.22	420	315	24.65	23.68	1.33
Cu	157	93	99.69	6.99	1.69	202	89	64.14	6.69	2.22	168	91	21.33	6.84	1.85	346	195	21.97	14.66	1.77
Zn	137	93	89.59	6.99	1.47	223	184	72.92	13.83	1.21	293	231	38.32	17.37	1.27	450	391	29.43	29.39	1.15
Pb	46	69	95.31	5.19	0.67	79	115	81.84	8.65	0.68	85	129	35.22	6.69	0.66	104	144	21.55	10.83	0.72
Cd	85	62	95.54	4.66	1.37	95	90	53.39	6.77	1.06	174	69	39.12	7.22	1.81	244	144	27.43	10.83	1.69
Hg	1.10	8.0	2.20	0.60	0.14	1.2	34.70	1.20	2.61	0.03	119	125.3	47.81	9.42	0.95	418.6	257.4	84.10	19.35	1.63

TABLE VI Mass balance data of M^{2+} taken up by (Al + Na) substituted tobermorite (prepared from Sodium meta-silicate and $AlCl_3 \cdot 6H_2O$) and the released Ca^{2+} solution after 2 h (reaction time)

Metal ion (M^{2+})	Initial concentration of M^{2+} (ppm)																			
	100					200					500					1000				
	M^{2+} uptake (meq/100mg)	Ca^{2+} release (meq/100mg)	Wt. % of M^{2+} uptaken	% of Ca^{2+} released	M/Ca Molar ratio	M^{2+} uptake (meq/100mg)	Ca^{2+} release (meq/100mg)	Wt. % of M^{2+} uptaken	% of Ca^{2+} released	M/Ca Molar ratio	M^{2+} uptake (meq/100mg)	Ca^{2+} release (meq/100mg)	Wt. % of M^{2+} uptaken	% of Ca^{2+} released	M/Ca Molar ratio	M^{2+} uptake (meq/100mg)	Ca^{2+} release (meq/100mg)	Wt. % of M^{2+} uptaken	% of Ca^{2+} released	M/Ca Molar ratio
Mn	156	54	85.64	4.12	2.88	198	84	54.35	6.41	2.35	181	92	19.87	7.02	1.96	82	87	4.50	6.63	0.94
Fe	66.7	28.8	37.22	4.48	1.13	184	173	51.34	13.19	1.06	314	294	35.04	22.42	1.07	950.2	903.3	53.02	68.89	1.05
Co	163	20	96.01	1.53	8.15	244	226	71.86	17.23	1.07	303	126	35.69	9.61	2.40	315	199	18.55	15.18	1.58
Ni	169	31	99.20	2.36	5.45	175	71	51.36	5.41	2.46	275	140	32.28	10.68	1.96	460	199	27.0	15.18	2.31
Cu	157	45	99.67	3.43	3.49	270	88	85.71	6.71	3.07	265	76	33.65	5.79	3.48	306	92	19.43	7.02	3.33
Zn	137	102	89.59	7.78	1.34	144	121	47.08	9.23	1.19	357	329	46.69	25.09	1.09	586	542	38.32	41.33	1.08
Pb	47	128	97.38	9.76	0.37	90	126	93.24	9.61	0.71	173	239	71.69	18.23	0.72	179	232	37.09	17.69	0.77
Cd	86	15	96.67	1.14	5.73	148	73	83.18	5.57	2.02	229	91	51.48	6.94	2.52	272	125	30.57	9.53	2.17
Hg	2.5	0.2	5.02	0.015	12.5	9.6	1.75	9.64	0.13	5.48	141	37.1	56.65	2.83	3.8	417	170.2	83.78	12.98	2.45

TABLE VII Mass balance data of M^{2+} taken up by (Al+K) substituted-tobermorite and the released Ca^{2+} in solution after 2 h (reaction time)

Metal ion (M^{2+})	Initial concentration of M^{2+} (ppm)																			
	100					200					500					**1000**				
	M^{2+} uptake (meq/100mg)	Ca^{2+} release (meq/100mg)	Wt. % of M^{2+} uptaken	% of Ca^{2+} released	M/Ca Molar ratio	M^{2+} uptake (meq/100mg)	Ca^{2+} release (meq/100mg)	Wt. % of M^{2+} uptaken	% of Ca^{2+} released	M/Ca Molar ratio	M^{2+} uptake (meq/100mg)	Ca^{2+} release (meq/100mg)	Wt. % of M^{2+} uptaken	% of Ca^{2+} released	M/Ca Molar ratio	M^{2+} uptake (meq/100mg)	Ca^{2+} release (meq/100mg)	Wt. % of M^{2+} uptaken	% of Ca^{2+} released	M/Ca Molar ratio
Mn	97	27	53.25	2.10	3.59	71	66	19.49	5.13	1.06	21	44	2.31	3.42	0.48	9.5	51	0.52	3.96	0.19
Fe	87.5	68.5	48.83	5.32	1.27	204	201.2	56.91	15.63	1.01	480.7	425	53.64	33	1.13	1157	1110	64.58	86.18	1.04
Co	154	86	90.71	6.76	1.79	203	99	59.78	7.68	2.05	159	144	18.73	11.18	1.10	105	154	6..18	11.96	0.68
Ni	99.8	110.5	58.58	8.85	0.90	103.7	118	30.43	9.16	0.88	125	144	14.67	1.18	0.87	260	110.5	15.26	8.58	2.35
Cu	71	31.5	45.09	2.45	2.25	69	30.6	21.91	2.38	2.25	83	44	10.54	3.42	1.88	86	94	5.46	7.30	0.91
Zn	135	82	88.29	6.37	1.64	135	82	88.29	6.37	1.64	211	201	27.59	15.61	1.05	375	358	24.52	27.80	1.05
Pb	48	38	99.46	2.95	1.26	51	56	52.84	4.35	0.91	51	74	21.13	5.75	0.69	60	78	12.43	6.06	0.77
Cd	67	30	75.31	2.33	2.23	114	33	64.07	2.56	0.42	143	40	32.15	3.11	3.57	157	56	17.65	4.35	2.80
Hg	0.80	24.5	1.61	1.90	0.03	2.2	61.6	2.21	4.78	0.36	146	143.7	58.66	11.16	1.02	213	156.3	42.79	12.14	1.36

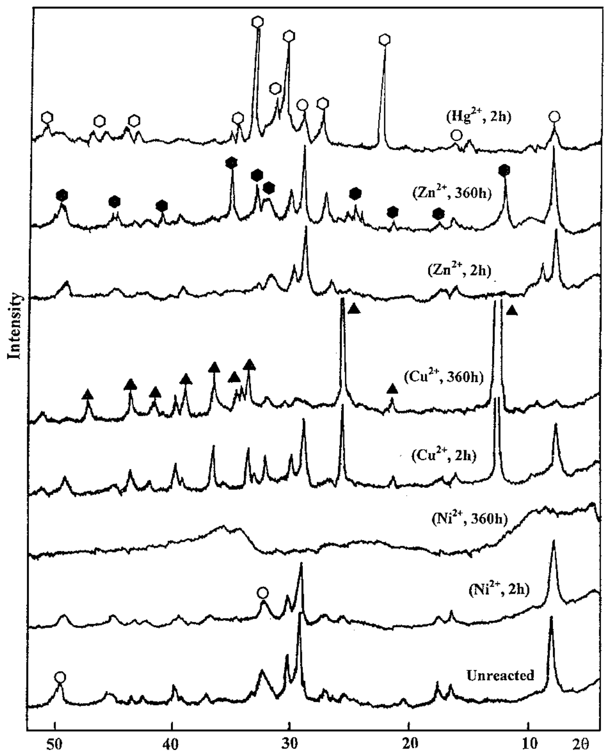


Figure 8 X-ray diffractograms of (Na + Al) substituted-tobermorite reacted with 1000 ppm solutions of for Ni^{2+}, Cu^{2+}, Zn^{2+} and Hg^{2+} for 2 and 360 hrs. (○ = Tobermorite, ▲ = Gerhardite ($Cu_2(OH)_3(NO_3)$ ⬢ = Rosasite ($ZnCO_3(OH)_2$), O = HgCO.2HgO).

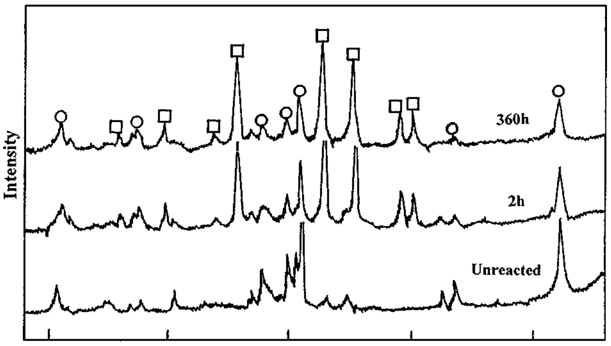


Figure 9 X-ray diffractograms of (Na + Al) substituted-tobermorite* reacted with 1000 ppm of pb^{2+} solution for 2 and 360 hrs. *Prepared from sod. meta silicate and $AlCl_3.6H_2O$ (○ = Tobermorite, □ = Hydrocerussite ($pb_3(CO_3)_2(OH)_2$).

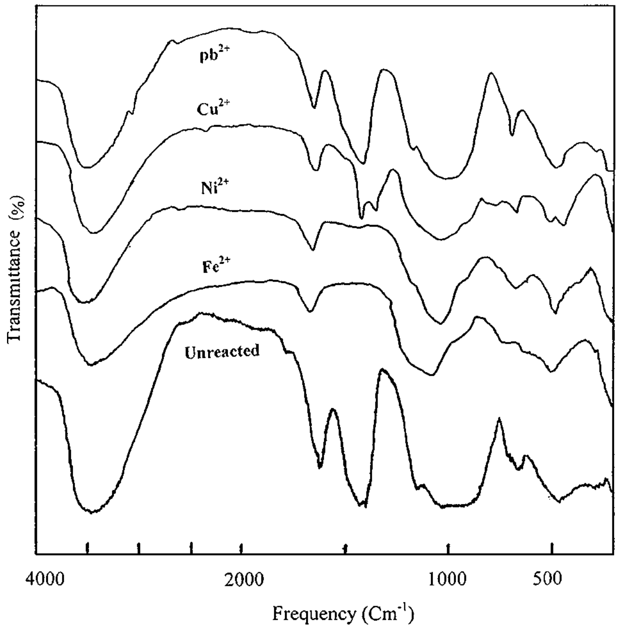


Figure 10 Change in relative intensities of infrared spectra bands of synthetic (Al + Na) substituted-tobermorite on reaction with Fe^{2+}, Ni^{2+}, Cu^{2+} and pb^{2+} solution for 360 h.

after 360 h i.e. led to amorphization. The crystallinity of the exchangers also does not completely remain intact i.e., poor crystallinity after the reaction with Mn^{2+}, Zn^{2+}, pb^{2+}, Cd^{2+} or Hg^{2+}. This is obvious from the decrease in relative intensities of d-spacing at 7.8 (2θ), 16 (2θ), 29.9 (2θ) and 31.8 (2θ) with respect to the reference materials. This was also reflected in the infrared spectral (Fig. 10). The most intense absorption band of tobermorite decreased, especially those located at 3500, 1450, 1060, 976 and 459 cm^{-1}.

The complete loss in crystallinity of the solids may be attributed mainly, to the acidic nature of the initial solutions (Table II). It was reported that [21] on reaction of tobermorite or xonotlite with Co^{2+} or Ni^{2+} partial Ca^{2+} exchange by Ni^{2+} or Co^{2+} did not lead to a loss of all crystallinity, while the total exchange led to its amorphization. But calcium silicate hydrates like tobermorites have a clearly defined crystalline from, their lattices are impure and contain an assortment of ions in solid solution [22]. This indicates that there is a certain basic stability of these crystalline structure in being able to accommodate the metal ions from the solution and still retain their basic crystalline from. It was suggested that [16–19] the metal ion uptake was primarily due to the breaking of Ca-O bonds from layered structure (Fig. 6) and this led to poor crystallinity of the solid and not amorphization even after 15-days from equilibrium. This behaviour was also noted in cases of Mn^{2+}, Zn^{2+}, pb^{2+} and Cd^{2+} (Figs 7–9).

The reaction of substituted tobermorites with Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, pb^{2+}, Cd^{2+}, and Hg^{2+} leads to precipitation of rhodochrosite [$MnCO_3$], goethite [$FeO(OH)_3$], gerhardite [Cu_2 $(OH)_3$ NO_3], rosasite [$Zn_2CO_3(OH)_2$], hydrocerussite [$pb_3(CO_3)_2$ $(OH)_2$] and [HgCO-2HgO] phases, respectively, as shown in XRD patterns (Figs 7–9). Precipitation of such phases requires a relatively basic medium. This was achieved from the liberation of hydrated Ca^{2+} and/or alkali metal ions from the lattice of the solids and this rises the pH-value (Table II).

Ca^{2+}-ions in solutions resulted from the partial exchange and partial hydrolysis of solid by acidic nature of metal ion solution. The first ($Ca^{2+} \Leftrightarrow M^{2+}$) may take place from the planar surface or edges of the solid. In this respect Komarneni, *et al.* [16] showed that by TEM and EDS, Ni was detected at the edge but not in the core on the reaction of tobermorite crystal with an uptake of 2.7 meq/Ni^{2+}/g. Their results indicated that the mechanism of reaction takes place from edge to core and the partial replacement led to amorphizations of the crystals in the rim only while almost complete replacement led to total amorphization. Precipitation of the previous mentioned phases during the reaction, will hinder, the complete exchange process and hence the ion uptake from solutions are mainly due to the immobilization (through the precipitation) and partially due to exchange $Ca^{2+} \Leftrightarrow M^{2+}$. Extra Ca^{2+} due to solid hydrolysis and precipitation of metal ions are responsible for the non-stoichiometric results which were obtained (Tables III–VII). Thus precipitation may be originated from hydrolysis of metal salt solution followed by carbonation.

The maximum ion uptake or Ca^{2+}-release have been detected in case of Fe^{2+} which could be related to the partial hydrolysis of the solid, due to the acidic nature of Fe^{2+} solution (pH = 2.87) and the basic nature of tobermorites, in spite of the fact that the ionic radii of Fe^{2+}, Co^{2+} or Ni^{2+} are approximately the same. The uptake of ions has been found to be in the following order: $Fe^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+} > Mn^{2+} > Hg^{2+} > Cd^{2+} > pb^{2+}$.

In calcium silicate frame work, it was reported that [11, 16, 17, 19] the ion uptake may arise as a result of the following steps: i- Broken bonds from edges, ii- Outer planar surface of the solid crystals, iii- Interlayer inclusion of cations for charge balance or iv- Reaction with structural calcium. It is not necessary that all these steps operate in any exchange reaction but at least one of them occurs during the exchange reaction. Komarneni *et al*. [16] considered that the term of exchange between solid and heavy metal solutions are due to net chemical change from solution and solid. But in some cases, the structure of the solid will change often from crystalline to amorphous (as in case of : Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} or Cu^{2+}) and hence the reaction of calcium silicate hydrate is not strictly analogous to traditional base exchange in zeolites and clays although in the latter there are minor structural changes with exchange of cations. Hereinafter, this phenomenon may refer to mixed effect between partial exchange and immobilization (precipitation), the latter is a major part of ion uptake where the cation uptake by the solids in some cases is greater than their CEC values. The partial exchange ($Ca^{2+} \Leftrightarrow M^{2+}$) and partial hydrolysis of the solids by acidic nature of the metal solutions led to a change in the molecular structure of some substituted-tobermorites, i.e. became amorphous.

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