Hydrothermal Synthesis and Transition Metal Cations Exchange Characterization of Titanium and [Titanium+Alkali Metals] Substituted-11Å Tobermorites

S. A. El-Korashy*

Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt.
(2003. 8. 28 접수)

요 약. 타이테늄과 [타이테늄 + 나트륨 (칼륨)]으로 치환된 11Å의 토버모라이트 고체가 180 ℃의 수열반응 조건하에서 합성되었고, 이 화합물은 Fe^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+}과 같은 중금속 양이온에 대해서 양이온 교환 성질을 보였다. 이 고체에 흡착된 중금속 양이온은 Fe^{3+} > Zn^{2+} > Cd^{2+} > Pb^{2+} 의 순서로 그 양이 감소하였고, 10% [타이테늄 + 칼륨]으로 치환된 토버모라이트가 최대값을 보였다. 총 양이온 교환능은 10% [타이테늄 + 칼륨]으로 치환된 토버모라이트와 타이테늄으로만 치환된 토버모라이트에 대해서 각각 71에서 89 meq/100 g와 50에서 56 meq/100 g로 측정되었다. 이 결과는 10% [타이테늄 + 칼륨]치환이 비치환 토버모라이트 보다 2.4배 이상의 양이온 교환능이 있음을 보여준다. 이는 교환체의 활성자리 수의 증가에 의한 것이다. 합성된 토버모라이트의 격자구조로의 타이테늄과 [타이테늄 + 나트륨 (칼륨)]의 포함은 각각 $Ti^{4+} \Leftrightarrow 2Ca^{2+}$와 $Ti^{4+} + 2Na^+ (K^+) \Leftrightarrow 3Ca^{2+}$의 치환에 의한 것이다. 합성과정 중 고체의 결정 격자로의 타이테늄과 [타이테늄 + 나트륨 (칼륨)]의 포함에 관한 메커니즘과 이들 고체에 의한 중금속 양이온 흡수가 연구되었다.

주제어: 11Å-토버모라이트, [타이테늄 + 나트륨] (칼륨) 치환 토버모라이트, 합성, 양이온 교환, 중금속 흡수

ABSTRACT. Titanium and [titanium+Na(K)] substituted 11Å tobermorites solids synthesized under hydrothermal conditions at 180 ℃ exhibit cation exchange properties toward heavy transition metal cations, such as Fe^{3+}, Zn^{2+}, Cd^{2+} and or Pb^{2+}. The amount of heavy metal cations taken up by these solids was found in the order: $Fe^{3+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$, and reached maximum at 10% [Ti-K]-substituted tobermorite. The total cation exchange capacity of the 10% Ti+Na (K) - substituted tobermorites synthesized here range from 71 to 89 meq/100 g, and 50-56 meq/100g for Ti-substituted only. Results indicated that 10% [Ti-K] substitution exhibit cation exchange capacity more 2.4 times than the unsubstituted-tobermorite. This is due to the increase of the number of active sites on the exchangers. The incorporation of Ti and/or [Ti-Na(K)] in the lattice structure of synthesized tobermorites is due to exchange of $Ti^{4+} \Leftrightarrow 2Ca^{2+}$ and or $Ti^{4+} + 2Na^+ (K^+) \Leftrightarrow 3Ca^{2+}$, respectively. The mechanism of Ti and [Ti-Na(K)] incorporations in the crystal lattice of the solids during synthesis and the heavy metal cations uptaken by these solids is studied.

Keywords: 11Å-Tobermorite, [Ti-Na] (K)-Substituted Tobermorite, Synthesis, Cation Exchange, Heavy Metals Uptake

INTRODUCTION

Various types of inorganic ion exchangers have been synthesized such as hydrous oxides and acid salts of multivalent metals, layered zirconium phosphates, hydroxyaptities, zeolites and aluminosilicates. These substances have been recognized for their potential applications due to low cost of synthesis and remarkable ion selective properties towards a large number of metal cations from their aqueous solutions. Applications include fertilizer production, water softening, catalysis or fixing of hazardous isotopes in cement and concrete matrix material.[1-8] Some authors have reported that a series of calcium silicate hydrate CSH[(*)] compounds prepared by hydrothermal treatment, act as cation exchanger with some divalent metal cations releasing Ca^{2+} and /or Si^{2+} lattice structure[3,9-19] and leading to their amorphization.[3,18,19]

11Å-tobermorite $(Ca_5Si_6O_{18}.4H_2O)$ is one of the major phases found in hydrothermally treated CaO-SiO_2-H_2O system. Furthermore, it has been found to be the major component of technically important autoclaved cement based products. Its crystal structure was first investigated by Megaw and Kelsey[20] and later by Hamid.[21] The basic layer structure consists of a central sheet of Ca^{2+} and O^{2-} ions which is sandwiched by rows of tetrahedral $SiO_2(OH)_2$ moieties that are linked to chains running parallel to the b-axis direction[22]. The presence of $\equiv Si-O-Si$ $\equiv$bridges between the chains has been confirmed by some authors,[23,24] According to ^{29}Si NMR studies,[25] the formation and structure of 11Å-tobermorite depends on the source of silica in the starting reaction.

It was reported [13,26,27] that ion exchange capacity increased in case of inserted $[Al^{3+}+Na^+]$ - ions in the crystalline lattice of tobermorite as isomorphous way.

The ion exchange properties of unsubstituted and substituted tobermorites fall into two categories: the reversible exchange as shown by alkali and alkali earth metal cations like Li^+, Na^+ K^+, Cs^+, Sr^{2+}, Ba^{2+} in $[Al^{3+}+Na^+]$- substituted tobermorites[3,13,28] and the irreversible type reactions shown by divalent metal cations like Ni^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} in unsubstituted tobermorite and other calcium silicate hydrate.[1,1,27,28]

Titanium is quite abundant in the earth's crust-occurring as the minerals rutile (a variation TiO_2), ilmenite $FeTiO_3$ and perovskite $CaTiO_3$. TiO_2 is the most widely used dioxide; because of its chemical intemees, it is used as a filler for plastics, dyes and rubbers.

This paper examins the ability of synthetic 11Å-tobermorites to accommodate Ti^{4+} and/or $[Ti^{4+}+Na^-$ $(K^+)]$- ions in their lattice structure during synthesis. The effect of their accommodation on cation exchange capacity (CEC) and heavy metal uptake of these solids have been studied in order to fully realize the potentialities of these inorganic exchangers during the treatment of various metal cations in aqueous solutions.

EXPERIMENTAL AND METHODS

Starting materials

The starting materials were mixtures of CaO with quartz (99.75% SiO_2, mean particle size less than 45 μ). CaO was prepared by ignition of British Drugs House (BDH) grade of $CaCO_3$ at 1050 °C for 3h. TiO_2, NaOH and KOH are BDH reagents grade were also used for synthesis of Ti-substituted and/or $[Ti+Na^+(K^+)]$-substituted 11Å-tobermorites.

Synthesis of 11Å tobermorites

Solid unsubstituted tobermorite was synthesized by mixing stoichiometric amount of CaO and SiO_2 at a molar ratio equal 0.83. Also 5 and 10% Ti-substituted tobermorites were synthesized by replace of 5 and/or 10% of the total weight of the dry mix with the overall CaO/SiO_2 molar ratio being 0.83. While $[(Ti^{4+}+Na^+$ and/or $K^+)]$-substituted-tobermorites were also prepared by the same previous ratios but in the presence of 1.0 M NaOH and/or KOH. Each solid mixture was added to 20 times of its weight of deionized water and stirred for 10 min. Each content was quantitatively transferred to a stainless steel autoclave bomb (250 cm^3) internally coated with Teflon. The autoclave was placed in a manually controlled electric heated oven, and the temper-

(*)-C–CaO, S–SiO_2, H–H_2O.

ature was raised gradually to 180°C and kept at this temperature for 24h. At the end of each run the autoclaved was cooled slowly until room temperature, and the content was washed with distilled water (20 ml) and dried at 60 °C for 48 h.

Cation exchange capacity (CEC) of the solids

The cation exchange capacity CEC (meq/100 g) of the synthesized solids were measured using a known method[30] as follows: 50 mg of each solid was repeatedly washed with 0.1 M KCl to saturate all the exchange sites with K^+, followed by removing excess KCl with 0.02 M KCl to prevent any hydrolysis (a correction was made for excess 0.02 M KCl which as determined by weighing), and displacing K^- ions from the exchange sites with for washing (30 min. equilibration time per washing) with 0.2M CsCl. The displaced K^1 was determined by atomic emission spectroscopy (AES) and the total CEC was estimated.

Cation exchange reaction experiments

CEC reaction experiments were conducted as follows: 20 mg of each solid were equilibrated for 24h in glass vials with 10ml of SO_4^{2-}, Cl^- or NO_3^- solution of 200-1000 ppm of Fe^{2+}, Zn^{2+}, Cd^{2-} or Pb^{2-}; SO_4^2 was used for Fe^{2-} or Zn^{2+}; Cl^- for Cd^{2+} and NO_3 for Pb^{2-}. After period of equilibration (24 h), 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 (ASS). The pH of the equilibrium solutions for reactions in the glass vials was immediately measured.

Characterization of the synthesized solids

The unsubstituted and ion-substituted tobermorite solids were dried at 60 °C for 48 h prior to characterization by X-ray diffraction (XRD) with Cu K_α radiation at a scanning speed of 1° min⁻¹, between 2θ=5 up to 55°, thermal analysis (Shimadzo Koto - Japan TDA) in the range of 25-1000°C at a sensitivity of ± 50 µV and with heating rate of 10° min⁻¹ were performed on some selected samples. A JEOL scanning electron microscope JSM-5600 attached
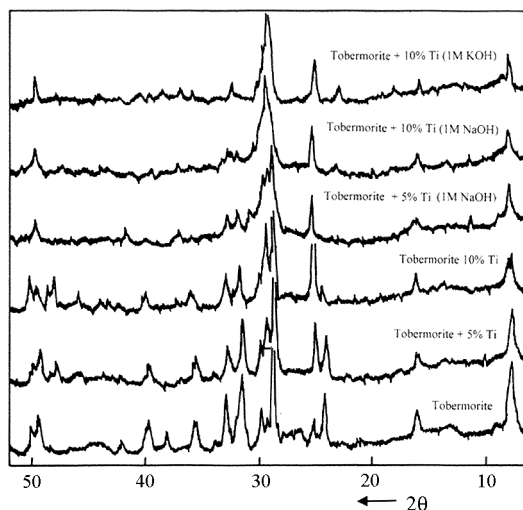

Fig. 1. XRD of synthesized unsubstituted and Ti+(Na⁺ and/ or K⁺) substituted 11Å-tobermorites.
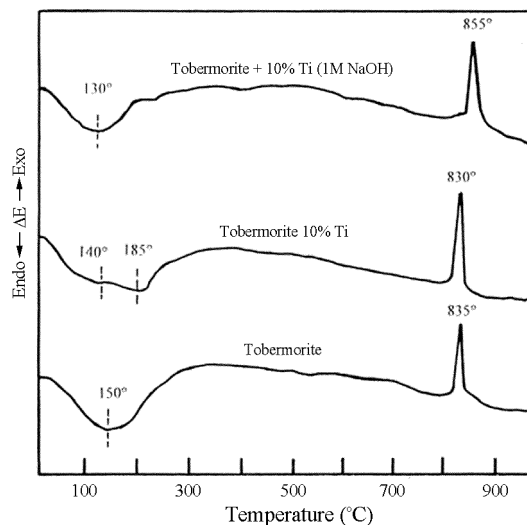

Fig. 2. DTA thermograph of synthesized 11Å-tobermorites.

with an energy dispersive X-ray (ISIS OXFORD) source was used for determining particle size, microstructure and chemical composition of the solids.

RESULTS AND DISCUSSION

Powder XRD analysis (*Fig.* 1) of the synthesized samples indicates the presence of one single phase of 11.3Å tobermorite in each of Ti-free, Ti and/or [Ti+Na (K)] solids. The results of scanning elec-
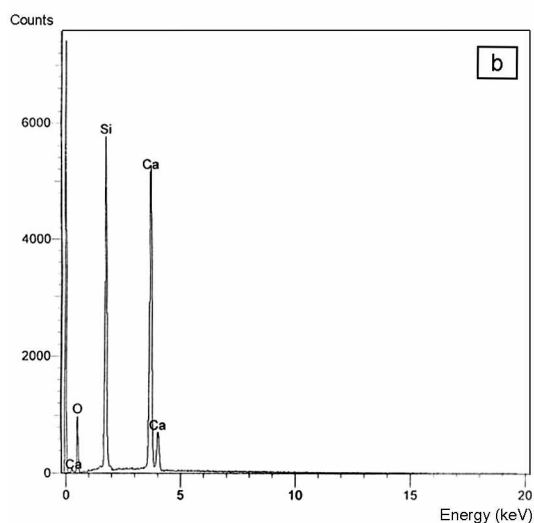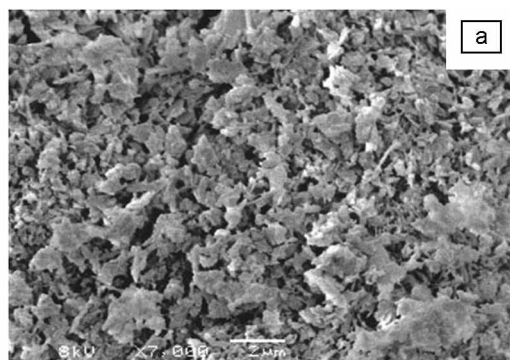
Fig. 3. (a) SEM of synthesized 11Å-tobermorite crystals; (b) EDAX of 11Å-tobermorite.

Fig. 4. (a) SEM of synthesized 10% Ti-substituted tobermorite; (b) EDAX of 10% Ti-Substituted tobermorite.

tron microscope (SEM) showed aggregates of round and plate crystals with some little differences in the particle size of unsubstituted, 10% Ti and [10% Ti+Na]-substituted tobermorites, respectively *Figs.* 3-5A. The crystallinity of the Ti-free tobertmorite sample was affected by substituting Ti^{4+} and/or [Ti^{4+}+Na^1 (K^1)] as shown in *Fig.* 1. The relative intensities of d-spacing at 7.8 (2θ), 16.1 (2θ), 29.9 (2θ), 31.8 (2θ) and 45.3 (2θ) decreased compared with the reference (Ti-free). This effect increase in the presence of Na^1 and/or K^1. This behaviors may be attributed to the increase of SiO_2 solubility in the presence of alkali metal hydroxides in the reaction mixture. The rate of tobermorite formation increase to indicate that the diffusion of SiO_2 is the rate determining step in the CSH formation.[15,16]
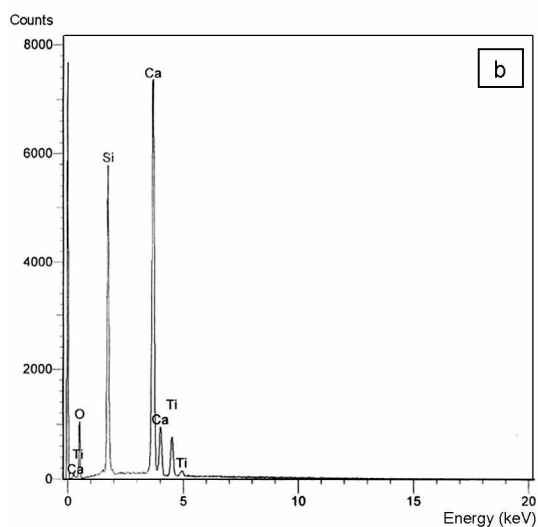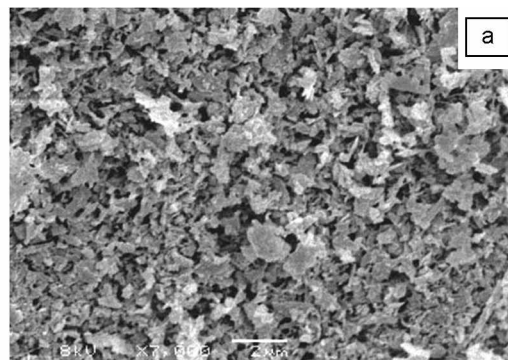
No considerable shifts were observed in the main (002) d-spacing (11.3Å) of tobermorites at 7.8 (2θ) *Fig.* 1. This indicates that Ti^{4+}-ions can not replaced by Si^{4+} in their lattice structures. This means that $Ti^{4+} \Leftrightarrow 2\ Ca^{2+}$ reaction is more favorable than that $Ti^{4+} \Leftrightarrow Si^{4+}$. In this respect it was reported[3] that Al^{3+}-ions can replace up to 15% of the Si^{4+} ions in the crystal structure of the tobermorite component. The incorporation or substitution of Si^{4+}-ions in tobermorite (isomorphous substitution) is accompanied by considerable shift in the main d-spacing (11.3Å) of tobermorites. There are also a linear correlation between the amount of Al^{3+} incorporated in the lattice structure and this shift. The substitution of Al^{3+}for Si^{4+} in tobermorite leads to a negative charge which could be balanced by positive ions
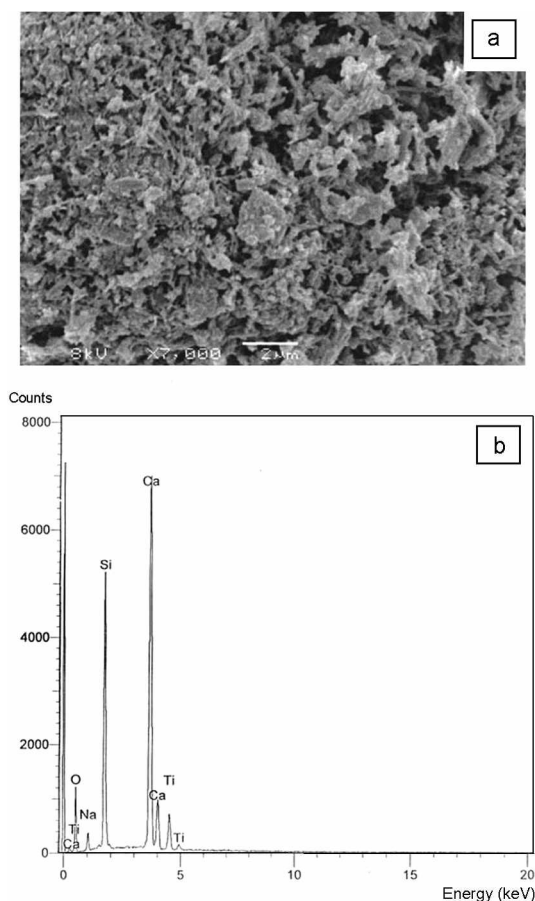
Fig. 5. (a) SEM of synthesized 10% Ti (in 1 M NaOH)-substituted tobermorite: (b) EDAX of 10% Ti (in 1 M NaOH)-Substituted tobermorite.

(such as H^+, Na^- and or K^-).

Al^{3+} replaces Si^{4+} in tobermorite due to the similarity in the coordination number in both cases (C.N =4). Ti^{4+} (in TiO_2) has a coordination number six corresponds to octahedral structure.[32] Since tobermorite has octahedral Ca[5] and Ca [6] *Fig.* 7 in very distorted sites[2], Ti^{4-} can be replaced by Ca^{2+} ($Ti^{4-} \Leftrightarrow 2Ca^{2+}$) and $Ti^{4+} + 2Na^+ (K^+) \Leftrightarrow 3Ca^{2+}$ in the case of [$Ti^{4-} +Na^+ (K^-)$]. In addition, it was observed[33] that Na^+-ions also can incorporated in the CSH compounds or tobermorite structure.

Thermal behavior (DTA) of unsubstituted tobermorite, 10% Ti^{4+} and 10% [$Ti^{4+}+Na^+$]- substituted tobermorites is shown in *Fig.* 2. Generally, little thermal changes have been found in the investi-gated samples. This indicates the formation of pure tobermorite phase. They show endothermic effects at lower temperatures, due to the loss of water of crystallization and exothermic effects at higher temperatures due to their crystallization into β-wollastonite.[27] These effects approximately do not occur at the same temperatures on their thermogram, and were affected by degree of crystallinity and substituted ions nature in crystal structure. Additionally, [Ti+Na]- substituted tobermorite exhibits more thermal stability than the others, due to the exothermic effect at 855 °C *Fig.* 2.

The energy dispersive analysis x-ray data (EDAX) of unsubstituted, 10% Ti^{4+} and 10% $Ti^{4+}+Na^+$ substituted-tobermorites *Figs.* 3-5b. *Fig.* 3b demonstrates the existence of K_α radiation of Ca and Si, while *Figs.* 4b and 5b demonstrate the existence of K_α radiations of Ca, Si & Ti and Ca, Si, Ti & Na respectively. This confirms the insert of Ti and/or Na-ions in the crystal structure of 11Å -tobermorites during their hydrothermal synthesis.

Results of cations exchange capacities (CEC) of the synthesized solids are shown in (*Table* 1). It was observed that unsubstituted 11Å-tobermorite reveals the lowest CEC value (37.2 meq/100 g). This indicates the extent of reversible exchange reaction.[11-16] For Ti- and/or [Ti+Na(K)]- substituted tobermorites the CEC values increased and reached maximum 89.4 meq/100 gm in case of 10% [Ti+K]-substitution. The value of 10% [Ti+K] substitution was found to be 2.4 times more than of unsubstituted solid, and 1.6 times more than 10% Ti-substituted. A 10% Ti-substituted also exhibites CEC 1.5 times more than the unsubstituted solid. Substituted 10% Ti exhibited a higher CEC value compared with Ti-free tobermorite due to $Ti^{4+} \Leftrightarrow 2Ca^{2+}$ exchange. In this respect, the ionic radius of Ti^{4-} (0.605Å) is less than the ionic radius of Ca^{2+} (0.99Å) and this substitution may create more cavities due to the resultant change of the structure: which increased by increasing the % of Ti-substitution. The presence of these cavities increases the number of active sites in the exchangers and this may be responsible for the increase of the measured CEC values. Increasing the number of cavities may cause solid structure
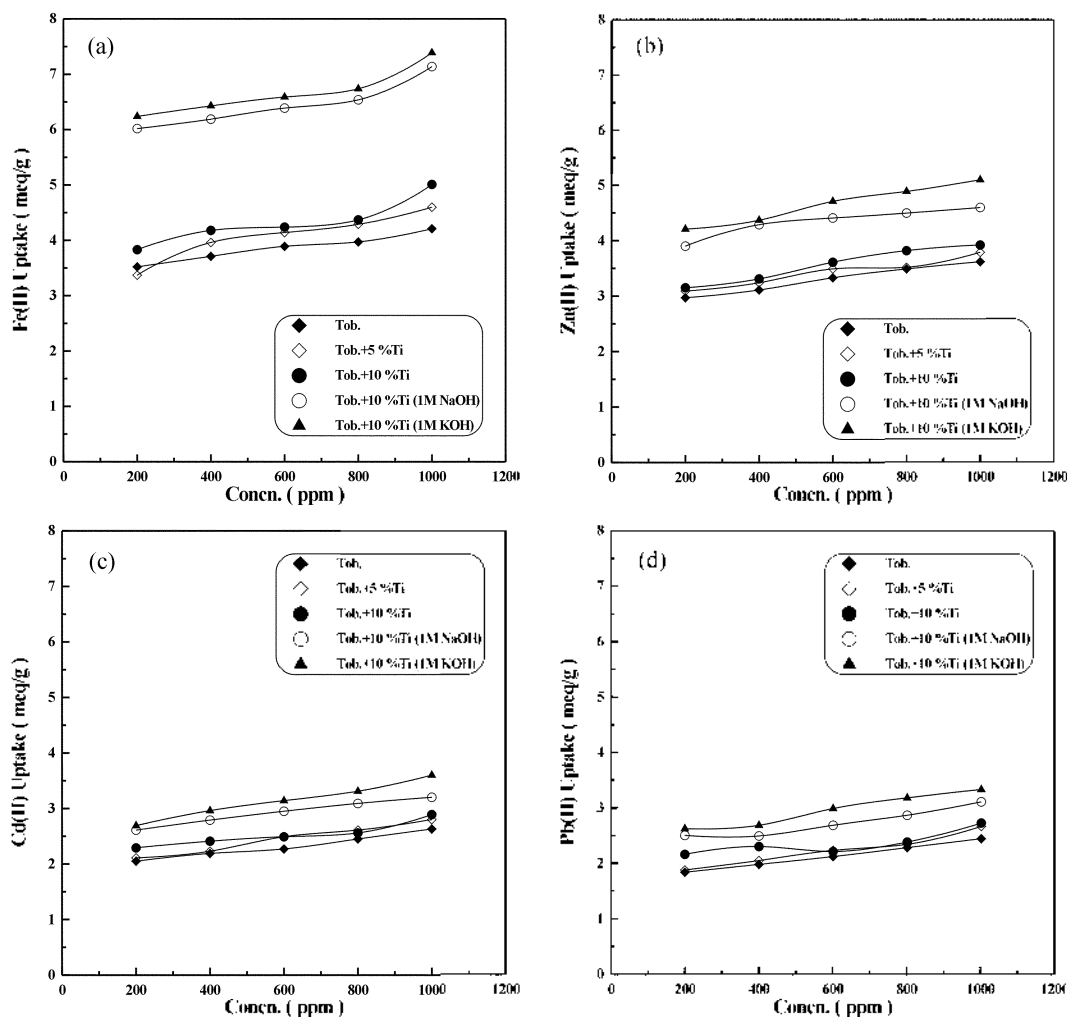
Fig. 6. (a-d) Heavy metals (II) uptake by solids at different concentrations.

deformation.

CEC value of [Ti⎮Na(K)]- substituted tober-morites, increase slightly in the presence of K⁺ compared with that in case of Na⁺. This may be attributed to the exchange of alkali metals in the inter layer of tobermorite structure.[27] Since K⁺ (or Na⁻) is less hydrated than Ca^{2+} and it can exchange faster. [Ti–K]-substituted realizes a CEC value is higher than that of [Ti+Na]-substituted (*Table* 1). This may be attributed to the fact that K⁺ is less hydrated ion than Na⁺.

Comparing CEC data of [Ti–K(Na)]-substituted tobermorites, in the present, study with [Al⎮Na]-substituted tobermorites reported in literature,[16,27,31]

demonstrates that the latter is higher than the former. This behavior may be attributed to the fact that the isomorphous replacement of Si^{4+} by Al^{3+} expanded the stacked Si/Ca/Si sheets in tober-morite structure with a basal d-spacing 11.3Å *Fig.* 7. This expansion was found to increase with increase of the Al^{3-} mol.%. There are also a linear correlation between the basal spacing and the degree of replacement of Si^{4-} by Al^{5+}. The greatest part of the incorporated Al^{3-} occurres between the Si-O-Si layers *Fig.* 7 of tobermorite[27]. The increase in the main d-spacing of 11.3Å to higher values may be due to the differences in ionic radii between Al^{31} (0.5Å) and Si^{4+} (0.4Å). But in the case of Ti^{41}
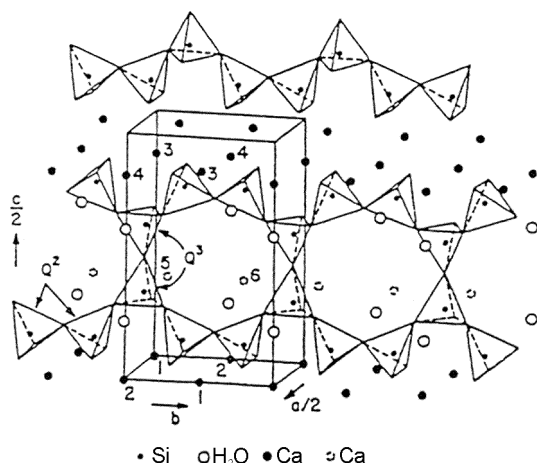
• Si ○H₂O ●Ca ⊙Ca

Fig. 7. A three-dimensional crystal structure view of anomalous 11.3Å-tobermorite.[27]

Table 1. Cation exchange capacity (CEC) (meq/100 g) of synthesized solids

Synthesized solid	CEC (meq/100 g)
Unsubstituted tobermorite	37.2
Tobermorite · 5% Ti	49.4
Tobermorite − 10% Ti	56.1
Tobermorite − 5% Ti (1MNaOH)	70.7
Tobermorite − 10% Ti (1MNaOH)	84.8
Tobermorite − 10% Ti (1MKOH)	89.4

incorporation in tobermorite during its synthesis, in the present study, showed none any of the above mentioned changes. This may be attributed to $Ti^{4+} \Leftrightarrow 2Ca^{2+}$ exchange process as discussed previously.

Results of pH-value change of the initial different cation metal solution in reaction with solids are given in *Table* 2. This change is attributed to the degree of release of Ca^{2+} and/or $K^{+}(Na^{+})$-ions from the structure of the solids.[15-17]

Results of the uptake of Fe^{2+}, Zn^{2+}, Cd^{2+} and/or Pb^{2+} by the synthesized solids are presented in *Fig.* 6(a-d). The amount of metal ions taken up by increases with the increase of the initial concentration of M^{2+}. The uptake of M^{2+} follows this order: $Fe^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$, and is attributed to $Ca^{2+} \Leftrightarrow M^{2+}$ exchange[16,27,30] and/or $Ca^{2+} + 2Na^{+}(2K^{+}) \Leftrightarrow 2M^{2+}$, because K^{+} (and/or Na^{+}) is less hydrated ions than Ca^{2+} it can be more easily substituted with M^{2+}. Hence, the M^{2+} taken up by the solids, generally, is found to be higher in the case of [Ti+K(Na)]-substituted tobermorites than that of unsubstituted tobermorite. In the case of Ti-substituted tobermorites the uptake increases by the increase of Ti^{4+}-ions substitutions, as shown in *Fig.* 6. The results amount of cation uptaken by the solids agree with the CEC data (*Table* 1).

The exchange in unsubstituted tobermorite was postulated[13,27] to take place from edge and planar surface sites and apparently from the interlayer Ca^{2+} sites, since tobermorite has octahedral Ca[5] and Ca[6] in very distorted sites where the Ca-O interaction is weak, *Fig.* 7. Hence, these are expected to be exchangeable with M^{2+}. On the other hand, the exchange of these hydrated ions is inhibited by their large radii, so that it has a low CEC value (*Table* 1).

In case of Ti and/or [Ti+Na(K)]- substituted tobermorites, $Ti^{4+} \Leftrightarrow 2Ca^{2+}$ process may create more additional cavities in the structure (due to the difference in ionic radius between them). These cavities may also accommodate more $Na^{+}(K^{+})$-ions in case of [Ti+Na(K)]-substituted tobermorites; and hence gave higher CEC (*Table* 1) or M^{2+} uptake (*Fig.* 6). The possibility of $Ti^{4+} \Leftrightarrow M^{2+}$ process may be here

Table 2. pH values of reacted metal solutions with solids for 24h

	Metal cation																			
	Fe^{2+}					Zn^{2+}					Cd^{2+}					Pb^{2+}				
	Conc. (ppm)																			
Solid	200	400	600	800	1000	200	400	600	800	1000	200	400	600	800	1000	200	400	600	800	1000
Free solid soln.	2.10	1.91	1.84	1.74	1.60	6.05	5.61	6.01	6.07	6.09	6.20	6.05	6.09	6.20	6.24	5.05	4.92	4.89	4.90	4.96
Uns. Tob.	3.02	2.31	2.11	1.95	1.85	6.91	6.72	6.47	6.37	6.29	7.18	6.59	6.24	6.41	6.31	6.37	6.39	6.21	5.24	6.29
5% Ti sub. Tob.	3.14	2.42	2.22	1.98	1.94	6.94	6.74	6.59	6.42	6.34	7.23	6.91	6.31	6.44	7.17	6.41	6.31	6.29	5.39	6.34
10% Ti sub. Tob	3.21	2.51	2.29	2.09	1.96	6.97	6.91	6.62	6.47	6.51	7.32	6.94	6.49	6.49	5.15	6.69	6.60	6.34	5.37	6.49
10% Ti + Na sub. Tob	3.56	2.67	2.37	2.21	2.09	7.03	6.99	6.69	6.59	6.55	7.59	7.08	6.62	6.58	7.29	6.78	6.51	6.50	5.49	6.27
10% Ti + K sub. Tob	3.72	2.72	2.47	2.32	2.14	7.09	6.98	6.74	6.62	6.59	7.62	7.04	6.72	6.66	7.41	6.83	6.55	6.62	5.61	6.21

excluded because the hydrated Ti^{4+} ions cannot exist in solution due to their high electric charges. The ratio between the ionic charge and ionic radius of Ti^{4+} is too high[32].

In conclusion 5 also 10% Ti and/or 10% [Ti+Na (K)]-substituted 11Å-tobermorites prepared under hydrothermal conditions at 180 °C for 24h, can be used as a cation exchangers for separating of heavy metals from their aqueous solutions. The amount of heavy metals taken up by the synthesized solids was found to be in this order : $Fe^{2+}>Zn^{2+}>Cd^{2+}>Pb^{2+}$, and reached maximum at 10% [Ti+K]-substitution. Ti^{4+}-ion can incorporate in the lattice structure of tobermorite solids during the synthesis. This is due to $Ti^{4+}\Leftrightarrow 2\ Ca^{2+}$ exchange process. The substitution of Ti^{4+} by Ca^{2+} and/or $Ti^{4+}+2Na^+\ (2K^+)\Leftrightarrow 3\ Ca^{2+}$ increases the number of active sites in the exchanger. The excess in active sites raises the cation exchange capacity of the concerned solids. The 10% substitution of Ti^{4+} increased the total exchange capacity of the synthesized solids 1.5-fold that of the unsubstituted ones. Moreover, 2.5-fold increase of the exchange capacity was observed as a result of 10% substitution of [Ti+K]. Indication thereby that the substitution of K contributed a 1.6 times increase in cation exchange capacity of the investigated solids.

REFERENCES

1. Suzuki, T.; Hatsuchika, T.; Miyake, M. *J. Chem. Soc. Faraday. Trans.* **1984**, *180*, 3157.

2. Komarneni, S.; Roy, D.M., Scientific Basis for Nuclear Waste Management, Brookins D. G. (ed.) Elsevier, New York, **1983**, *5*, 55.

3. Shrivastava, O.P.; Komarneni, S. *Cem. Concr. Res.*, **1994**, *24*(3), 573.

4. Macias, A.; Kindness, A.; Glasser, F. P. *Cem. Concr. Res.*, **1997**, *27*(2), 215.

5. Bagosi, S.; Csetenyi, L. J. *Cem. Concr. Res.*, **1998**, *28*(12), 1753.

6. Sandor, B.; Laszlo, J. C. *Cem. Concr. Res.*, **1999**, *29*, 479.

7. El-Korashy, S. A. *J. Mater. Sci.* **2003**, *38*, 1709.

8. Lena, Q. M. A.; Gad, N. R.. Water, Air and Soil Pol-

lution. **1999**, *110*, 1.

9. Komarneni, S., Nucl. Chem. Waste Manage. **1985**, *5*(4), 247.

10. Komarneni, S.; Breval E.; Roy, D.M.; Roy, R. *Cem. Concr. Res.* **1988**, *18*, 204.

11. Labhestwar, N.; Shrivastava, O. P. *Ind. J. Chem. Soc.* **1989**, *27A*(11), 999.

12. Labhestwar, N.; Shrivastava, O.P., React Solids, **1989**, *7*(3), 225.

13. Tsuji, M.; Komarneni, S. *J. Mater. Res.* **1989**, *4*(3).

14. El-Korashy, S. A., Monatshefte für Chemie, **1997**, *128*, 599.

15. El-Korashy, S. A.; Al-Wakeel, E. I. *Egypt J. Chem.*, **1999**, *42*(3), 237.

16. Al-Wakeel, E. I., El-Korashy, S. A.; El-Hemaly, S. A.; Rizk, M. A. *J. Mater. Sci.* **2001**, *36*, 2405.

17. El-Korashy, S. A. Monatshefte für Chemie, **2002**, *133*(3), 333.

18 Siau Ciunas. R.; Palubinskaite, D. Kondratiene, D. Mater. Sci. (Medziagotyra), **2001**, *7*(3), 177.

19. El-Korashy, S. A., accepted for publication in J. of Ion Exange (Japan) (In press).

20. Megaw, H. D.; Kelsey, C. H. Nature (London), **1956**, *177*, 390.

21. Hamid, S. N., Kristallogr Z. **1981**, *145*, 189.

22. Komarneni, S.; Tsuji, M. *J. Amer. Ceram. Soc.*, **1989**, *72*(9), 1668.

23. Komarneni, S.; Roy, R.; Roy, D. M.; Fyfe, C. A.; Kennedy, G. J.; Bothner, A. A.; Dadok, J.; Chesnick, A. S. *J. Mater. Sci.* **1985**, *20*, 4209.

24. Okada, Y.; Ishida, H; Mitsuda, T. *J. Amer. Ceram. Soc.* **1994**, *76*(3), 765.

25. Pkada, Y.; Isu, N.; Masuda, T.; Ishida, H. *J. Ceram. Soc. Japan*, **1994**, *102*(12), 1148.

26. Tsuji, M.; Komarneni, S.; Malla, P. *J. Amer. Ceram. Soc.*, **1991**, *74*(2), 274.

27. El-Korashy, S. A.; Al-Wakeel, E. I., El-Hemaly, S. A.; Rizk, M. A. *Egypt J. Chem.*, **2002**, *45*(4), 723.

28. Tsuji, M.; Komarneni, S. *J. Amer. Ceram. Soc.* **1989**, *72*, 1668.

29. Komarneni, S; Roy, D. M.; Roy, R. *Cem. Concr. Res.*, **1986**, *16*, 47.

30. El-Korashy, S. A. *J. Korean Chem. Soc.*, **2002**, *46*(6), 515.

31. Al-Wakeel, E. I.; El-Korashy, S. A. *J. Mater. Sci.*, **1996**, *31*, 1909.

32. Lee, J. D. "Concise Inorganic Chemistry, **1991**, 4th edn. Chapman & Hall. London, P. 48.

33. Wieslawa, N. W., *Cem. Concr. Res.* **1999**, *29*, 1759.