

Characterization of Cation Exchange and Cesium Selectivity of Synthetic Beta-Dicalcium Silicate Hydrate

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요 약. 240 °C와 Ca:Si=2 몰 비율의 열수상태에서 합성된 고체 베타-디칼슘 실리케이트 하이드레이트(β -C₂SH)는 Fe, Cu, Zn, Cd, 및 Pb와 같은 2가 금속 양이온에 대한 양이온 교환 성질을 보여준다. 그 고체에 의한 금속 양이온 흡인력은 Fe²⁺ > Cu²⁺ > Zn²⁺ > Cd²⁺ ≈ Pb²⁺의 순서로 뒤이 밝혀졌다. 고체에 세슘 선택성은 Li⁺, Na⁺ 및 K⁺와 같은 1가 양이온이나 Ca²⁺, Mg²⁺ 및 Ba²⁺와 같은 2가 양이온이 Cs⁺보다 백배이상 진한 상태에서 나타내었다. Cs⁺의 흡인력은 Mg²⁺의 존재하에서 최대치를 보여주었고, 반면에 K⁺의 존재하에서 최소치를 보여주었다. 2가 금속이온에 대한 β -C₂SH의 다른 친화도는 이들 이온을 분리하는데 사용할 수 있다. 또한 β -C₂SH에 의한 금속 양이온 교환에 대한 반응경로 및 세슘 선택성이 연구되었다.

주제어: 베타-디칼슘 실리케이트 하이드레이트, 중금속, 양이온 교환, 이온 흡수, 세슘 선택성

ABSTRACT. Solid beta-dicalcium silicate hydrate (β -C₂SH) synthesized under hydrothermal conditions at 240 °C and Ca:Si=2 molar ratio shows cation exchange properties towards divalent metal cations such as Fe, Cu, Zn, Cd, or Pb. The ability of metal cation uptake by the solid was found to be in the order: Fe²⁺ > Cu²⁺ > Zn²⁺ > Cd²⁺ ≈ Pb²⁺. Cesium selectivity of the solid was demonstrated in the presence of univalent cation such as Li⁺, Na⁺ and K⁺ and divalent cations such as Ca²⁺, Mg²⁺ and Ba²⁺, which are one hundred times more concentrated than the Cs⁺. The uptake of Cs⁺ is maximum in the presence of Mg²⁺ whereas it is minimum in the presence of K⁺. The different affinities of β -C₂SH towards divalent metal cations can be used for the separation of those ions. Due to its selectivity for cesium it can be used in partitioning of radioactive Cs⁺ from nuclear wastes containing numerous cations. The mechanism of the metal cation exchange and cesium selectivity reactions by the solid is studied.

Keywords: Beta-dicalcium silicate hydrate, Heavy metals, Cation exchange, Ion uptake, Cesium selectivity

INTRODUCTION

Various types of inorganic materials act as cation exchangers such as layered zirconium phosphates, clay minerals, hydroxyapatites, and frame-work aluminosilicates. These materials have been recognized for potential applications due to their low cost

of preparation and remarkable ion selective properties towards a large number of metal cations from solution. The applications vary from their use in water softening, fertilizer, catalysis to fixing of hazardous isotopes in cement and concrete matrix materials.¹⁻⁹ Some authors have reported that some calcium silicate hydrate compounds prepared under

hydrothermal treatment, mainly 1.1 nm-tobermorites, 1.1 nm-ion substituted tobermorites, xonotlite and CSH^{*1} (I), act as cation exchanger with some metal cations with Ca^{2+} or Si^{4+} in their lattice structures^{3,7-15} and leading to their amorphization.^{3,14,15}

Beta-dicalcium silicate hydrate ($\beta\text{-C}_2\text{SH}$) ($\text{Ca}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$) occurs in nature, usually as a white fibrous mineral known as hillebrandite.¹⁶ Synthetic $\beta\text{-C}_2\text{SH}$ was prepared from a mixture of tricalcium silicate and silicic acid¹⁷ as well as silica¹⁸ by means of hydrothermal process. On heating, $\beta\text{-C}_2\text{SH}$ starts to decompose at about 500 °C and produces poorly crystalline and chemically pure $\beta\text{-C}_2\text{S}$ that is stable at room temperature without the addition of any chemical stabilizers.¹⁸ $\beta\text{-Ca}_2\text{SiO}_4$ is considered as one of the important constituent compounds of portland cement and generally synthesizes by high-temperature solid state reaction of CaO and SiO_2 at about 1400 °C.

Powder X-ray diffraction (XRD) studies of natural¹⁹ and synthetic [18] $\beta\text{-C}_2\text{SH}$ revealed a monoclinic structure, but recent studies by Youn *et al.*¹⁹ suggested that the crystal structure of $\beta\text{-C}_2\text{SH}$ may be triclinic, rather than monoclinic symmetry and analogous analogy with wollastonite ($\text{CaO} \cdot \text{SiO}_2$) compound. Results of silicate anion structure of synthetic $\beta\text{-C}_2\text{SH}$ reported by Ishida *et al.*¹⁸ using ²⁹Si MASNMR technique showed that single drierkette (single chains containing three tetrahedra per unit cell) appeared single chemical shift at -86.5 ppm Q².

The objectives of this work here are (a) to determine the cation exchange capacity of synthetic $\beta\text{-Ca}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ prepared under hydrothermal treatment toward some heavy metal cations and (b) to determine the cesium [Cs^{137}] selectivity of this solid from different solutions containing alkali and alkaline earth cations. This work was undertaken in order to fully realize potentialities of this inorganic cation exchanger for the treatment of various metallic cations in solutions and nuclear waste (as cesium) disposal areas.

EXPERIMENTAL AND METHODS

Starting Materials

The starting materials were mixtures of CaO with quartz (99.75% SiO_2 mean particle size below 45 μm). The CaO was made from CaCO_3 (BDH reagent - grade) by heating at 1050 °C for 3 h.

Synthesis of $\beta\text{-C}_2\text{SH}$

Solid $\beta\text{-C}_2\text{SH}$ was synthesized by mixing stoichiometric amounts of CaO and quartz at a molar ratio equal to two. The solid was added to 20 times of its weight of decarbonated deionized water and stirred for 15 min. The 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 electrically heated oven, and the temperature was raised gradually to 240 °C and kept at this temperature for 6-days. At the end of the run the autoclave was cooled slowly until room temperature, and the content was washed with distilled water (10 ml) and dried at 80 °C for 24 h. The solid was characterized by X-ray powder diffraction, SEM, with EDAX, DTA-TG and FTIR spectroscopy and chemical analysis.

Cation exchange capacity (CEC) of $\beta\text{-C}_2\text{SH}$

The CEC (meq/gm) of $\beta\text{-C}_2\text{SH}$ solid was determined by using the method reported previously.¹⁴ The procedure can be briefly described as follows: 50 mg of the solid was washed twice (equilibration time was 30 min. for each washing) with KCl to saturate all the exchange sites with K^+ , followed by washings with 0.02N KCl five times to remove the excess of KCl to prevent hydrolysis. The K^+ ions from the exchange sites were displaced by washings (30 min. equilibration time per washing) with 0.2N CsCl four times. The solution was collected and analyzed for K^+ by AES and the total CEC was determined.

Cesium selectivity in the presence of alkali and alkaline earth cations

The selective exchange was measured by the following procedure reported in [3]: 25 ml of 0.02N chloride solutions of M^{II} (Li, Na, K, Mg, Ca or Ba) containing 2×10^{-4} N CsCl was added to 25 mg of $\beta\text{-C}_2\text{SH}$ solid in 50 ml glass bottle. The mixture

* $\text{C}=\text{CaO}$, $\text{S}=\text{SiO}_2$, $\text{H}=\text{H}_2\text{O}$.

was equilibrated for 24 h at 25 °C. Triplicates were used for each cation. After equilibration, the solid and solution were separated. The concentration of cesium ion was analyzed by atomic absorption spectroscopy (AAS) using Perkin-Elmer PE 703 instrument.

Cation exchange reaction experiments

CEC reaction experiments were conducted as follows: 20 mg of each solid were equilibrated for different periods (1-24 h) in glass vials with 10 ml of Cl^- , SO_4^{2-} or NO_3^- solution of 200, 400, 800 or 1000 ppm of Fe^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} or Pb^{2+} ; NO_3^- was used for Pb^{2+} ; Cl^- for Cd^{2+} and SO_4^{2-} for Cu^{2+} , Fe^{2+} or Zn^{2+} . After different periods of equilibration, the solid phases in the glass vials were separated by centrifugation, and a part of the supernatant solution was collected for chemical analysis using AAS. The pH of the equilibrium solutions for each reaction in the glass vials was immediately measured.

Characterization of the solids

The $\beta\text{-C}_2\text{SH}$ exchanger and the solids after exchange reactions were dried at 60 °C in oven for 24 h and characterized by DTA-TG Perkin-Elmer 7 series thermal analysis system in the range 50-1100 °C using a heating rate of 10°/min. XRD a Scintag/AVX 3100 XRD system with CuK_α radiation and FTIR using NiColet FT-IR Magna-IR 560 were used. A JEOL scanning electron microscope JSM-5600 attached with an energy dispersive X-ray (ISIS OXFORD) source was used for determining particle size, microstructure and chemical composition.

RESULTS AND DISCUSSION

Powder XRD analysis (Fig. 1) showed that one single phase of $\beta\text{-C}_2\text{SH}$ formed with matches ASTM card no. 11-594. This phase consisted of aggregates of fibrous crystals as examined by SEM (Fig. 2) and decomposes in the range of 490-660 °C as determined by DTA-TG (Fig. 3) and forms $\beta\text{-C}_2\text{S}$.

The chemical composition and cation exchange capacity (CEC) of $\beta\text{-C}_2\text{SH}$ are given on Table 1.

The total value of CEC of $\beta\text{-C}_2\text{SH}$ based on K^+ exchange is 0.287 meq/g and represents the extent of reversible exchange reaction.

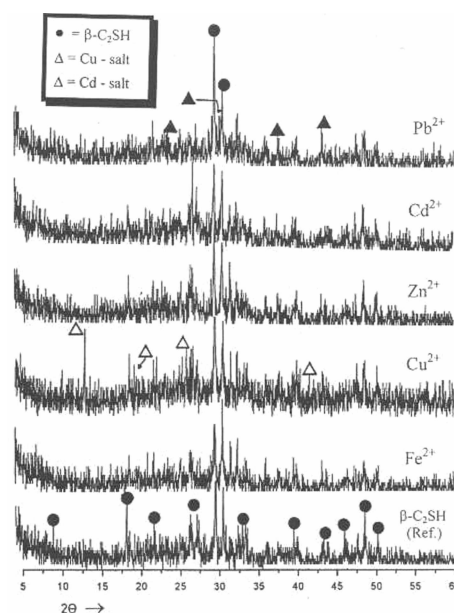


Fig. 1. XRD patterns of $\beta\text{-C}_2\text{SH}$ reacted with 1000 ppm of Fe^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} or Pb^{2+} for 24 h.

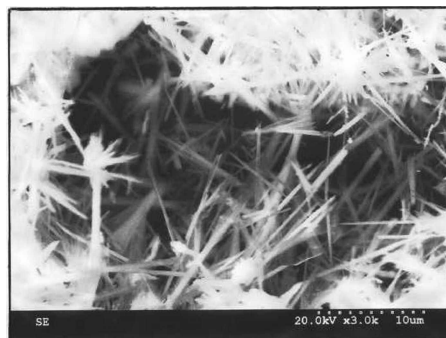


Fig. 2. SEM Photographs of synthesized $\beta\text{-C}_2\text{SH}$ crystals.

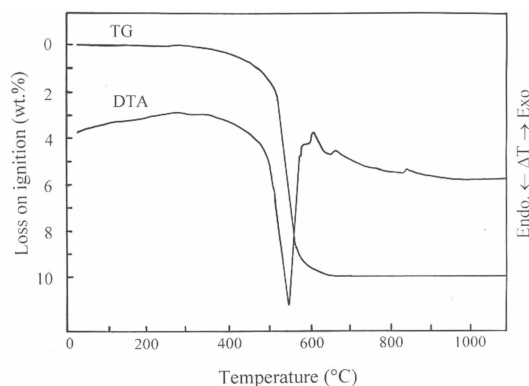


Fig. 3. Thermal analysis of $\beta\text{-C}_2\text{SH}$ by TG-DTA.

Table 1. Chemical composition and CEC of β -C₂SH

Solid	Chemical composition	CEC meq/g
β -C ₂ SH	Ca _{2.01} Si _{0.98} O _{3.97} ·1.03H ₂ O	0.287

Table 2. Cs⁺ selectivity (meq/g) and distribution coefficient from different cationic solution

Metal ion mixture	Cs ⁺ taken up (meq/g)	K _d
Cs / Mg	0.2289	3667
Cs / Li	0.2115	14973
Cs / Ca	0.2077	10055
Cs / Na	0.1576	18181
Cs / Ba	0.1205	9440
Cs / K	0.0823	9055

Cesium selectivity values in the presence of different competing cations are shown in Table 2 and they increase as follows: Mg>Li>Ca>Na>Ba>K.

The maximum selectivity uptake of Cs⁺ is about 0.23 meq/g in the presence of Mg²⁺ whereas it is minimum in the case of K⁺ ions. This shows that the K⁺ is the most competing and Mg²⁺ is the least competing with Cs⁺ toward the exchanger. The distribution coefficient (K_d) for Cs⁺ between the exchanger and solution phase of Mⁿ⁺ (n=2 or 1) was calculated using Eq. (1) [3]:

$$K_d = \frac{\text{fraction of cation on ion exchanger}}{\text{fraction of cation in solution}} \times \frac{\text{ml of solution}}{\text{g of ion exchanger}} \quad (1)$$

An examination of cesium selectivity (Table 2) shows that the uptake is related to the hydration sta-

tus of the cations. Highly hydrated Mg²⁺ and Li⁺ ions are excluded while less hydrated Cs⁺ and K⁺ are preferentially taken on the surface of β -C₂SH structure. In this respect, Shrivastava *et al.*³ considered that Cs⁺ selectivity (in the presence of alkali metals) by synthetic (Na+Al)-tobermorites depends upon hydration status of the concerned cation and the steric limitation of tobermorite structure. The uptake of Cs⁺ is reversible ion exchange reaction²⁰ resulting in release of equivalent Na⁺ from the inter-layers of tobermorite or Ca²⁺ in case of unsubstituted tobermorite.

The pH-value of the initial cation metal solutions varied with the type of salt (Table 3). This change is attributed to the degree of release of Ca²⁺-ions from the structure of the β -C₂SH solid in solution to from hydrate calcium ions during the reaction.¹²⁻¹⁵

Results of the exchange reaction of Fe²⁺, Cu²⁺, Zn²⁺, Cd²⁺ or Pb²⁺ with Ca²⁺ in β -C₂SH are presented in Figs. (4-8). Generally, the amount of metal ions taken up by β -C₂SH increases with increasing reaction time and/or initial concentration in the order: Fe²⁺>Cu²⁺>Zn²⁺>Cd²⁺≈Pb²⁺.

In these reactions the exchange of Ca²⁺↔M²⁺ was found to be non-stoichiometric. Generally, the uptake of M²⁺ by the solids was higher than Ca²⁺-ions released, with increasing reaction time or metal ion concentration (Figs. 4-8).

The non-stoichiometry arises from limited partial hydrolysis of β -C₂SH silicate chains (Fig. 9). This is due to the acidic nature of the M²⁺-solutions, especially in the case of Fe²⁺, Cu²⁺ or Pb²⁺ ions (Table 3)

Table 3. pH values of reacted metal solutions

Reaction time h	Metal Cation																			
	Fe ²⁺				Cu ²⁺				Zn ²⁺				Pb ²⁺				Cd ²⁺			
	200	400	800	1000	200	400	800	1000	200	400	800	1000	200	400	800	1000	200	400	800	1000
0	2.04	1.87	1.69	1.53	5.03	4.76	4.57	4.41	6.01	5.54	6.05	6.09	5.01	4.80	4.91	4.95	6.17	6.01	6.18	6.25
1	2.45	2.04	1.89	1.68	9.40	5.81	5.05	4.75	6.80	6.65	6.41	6.37	6.40	6.35	6.09	6.60	7.16	6.62	6.43	6.35
6	2.54	2.44	1.94	1.82	9.59	6.77	5.08	4.85	6.78	6.59	6.44	6.37	7.29	5.86	6.00	6.09	7.18	7.30	7.14	7.20
12	2.69	2.56	2.10	1.95	9.45	5.83	5.25	4.95	6.87	6.68	6.43	6.40	8.05	9.43	6.05	6.79	7.60	7.25	7.12	7.00
24	2.98	2.69	2.24	2.05	9.43	5.88	5.29	4.97	6.97	6.79	6.49	6.38	7.58	9.57	7.51	6.04	6.65	6.54	6.45	6.44

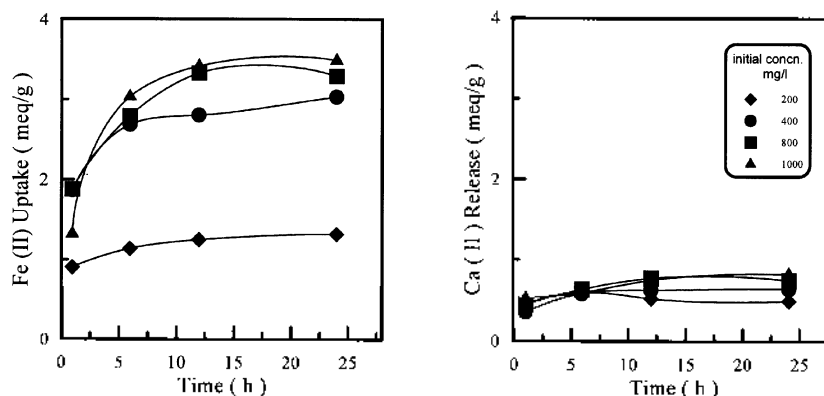


Fig. 4. Effect of concentration and time on Fe(II) uptake and Ca(II) from β -dicalcium silicate hydrate.

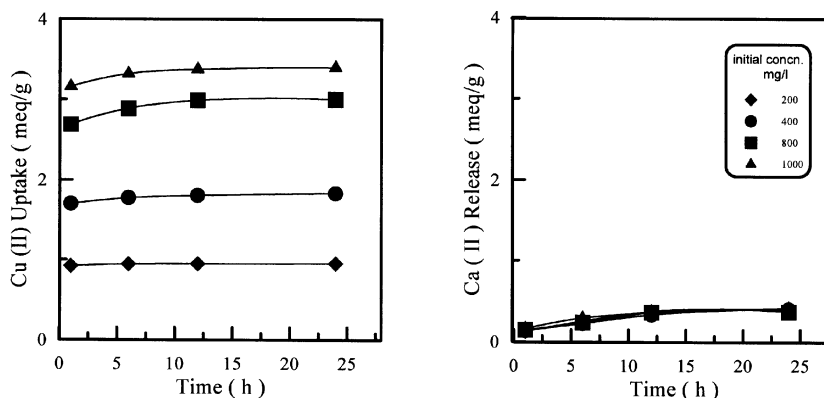


Fig. 5. Effect of concentration and time on Cu(II) uptake and Ca(II) from β -dicalcium silicate hydrate.

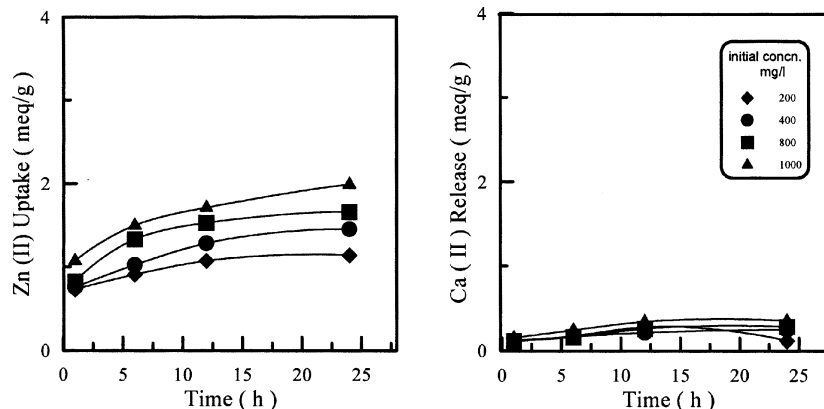


Fig. 6. Effect of concentration and time on Zn(II) uptake and Ca(II) from β -dicalcium silicate hydrate.

and the basic nature of the solid. Accordingly, extra Ca^{2+} -ions and little amounts of (meq/g) of Si^{4+} were detected in solutions. Part of the total Ca^{2+} ions liberated from structure reacted with free SO_4^{2-} (in case

of Fe, Cu and/or Zn salts) to form insoluble CaSO_4 , which was confirmed by measuring the free SO_4^{2-} after the reaction. The remaining Ca^{2+} -ions apparently exchanged with metal ions ($\text{Ca}^{2+} \leftrightarrow \text{M}^{2+}$). On

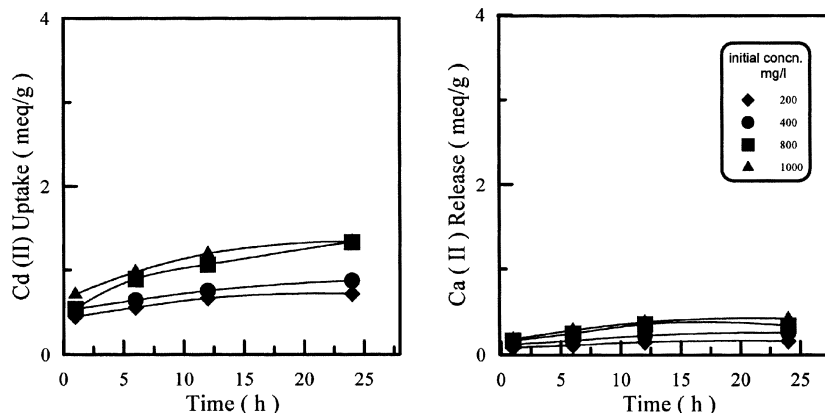


Fig. 7. Effect of concentration and time on Cd(II) uptake and Ca(II) from β -dicalcium silicate hydrate.

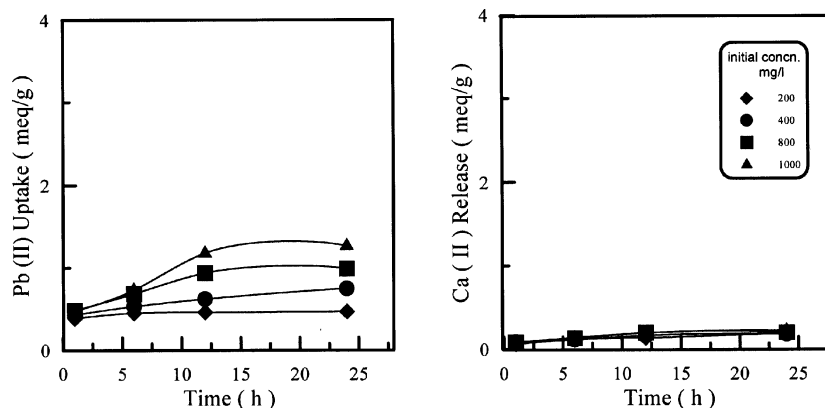


Fig. 8. Effect of concentration and time on Pd(II) uptake and Ca(II) from β -dicalcium silicate hydrate.

the other hand Si^{4+} was measured by molybdenum blue photo-metric method,¹² so that it is difficult to draw precisely the relationship between the exact amounts of Ca^{2+} exchanged with M^{2+} .

In addition, some of these cations, such as Cu^{2+} and Cd^{2+} formed precipitates which were detected by XRD (Fig. 1), while no precipitates were detected with Fe^{2+} , Zn^{2+} and Pb^{2+} by XRD. This may be in amorphous state as in precipitation of Zn^{2+} on the surface of $\beta\text{-C}_2\text{SH}$ crystals as shown in SEM micrograph (Fig. 10a) and confirmed by EDAX (Fig. 10b). All the above factors are responsible for non-stoichiometry of $\text{Ca}^{2+} \leftrightarrow \text{M}^{2+}$ exchange as shown in Figs. 4-8.

The reaction of these cations leads to a partial loss of crystallinity of $\beta\text{-C}_2\text{SH}$ as can be deduced from the decrease of the relative intensities of d-spacing as can be seen in case of Fe^{2+} and Cd^{2+} with

respect to the reference (Fig. 1).

The exchange reaction mechanism ($\text{M}^{2+} \leftrightarrow \text{Ca}^{2+}$) in $\beta\text{-C}_2\text{SH}$ may take place between M^{2+} and Ca^{2+} which is on the surface and edge sites linked with Si-O chains (Fig. 9) as in case of CSH(I)¹⁵ or tobermorite ($\text{Ca}_3\text{Si}_6\text{H}_4$) [8,13,14]. In the latter, the basic layer structure consists of double layers silicate anions, while $\beta\text{-C}_2\text{SH}$ has a single chain structure (Fig. 9).¹⁸

The metal ions uptake phenomenon by the $\beta\text{-C}_2\text{SH}$ solid appears to be from both partial exchange ($\text{Ca}^{2+} \leftrightarrow \text{M}^{2+}$) and immobilization (precipitation). So it is difficult to delineate the extent of cation exchange from the precipitation of these cations during the course of reaction. Precipitation of these cations as salts on the surface of $\beta\text{-C}_2\text{SH}$ as in the case of Cu^{2+} and Cd^{2+} (as detected by XRD, Fig. 1) and Zn^{2+} (as

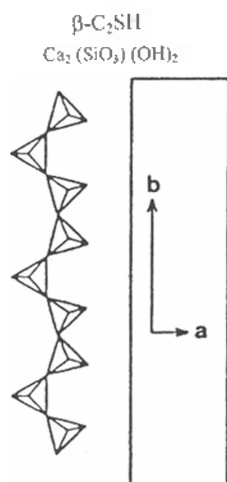


Fig. 9. Schematic diagram shows the single drierite anion structure of $\beta\text{-C}_2\text{SH}$ [18].

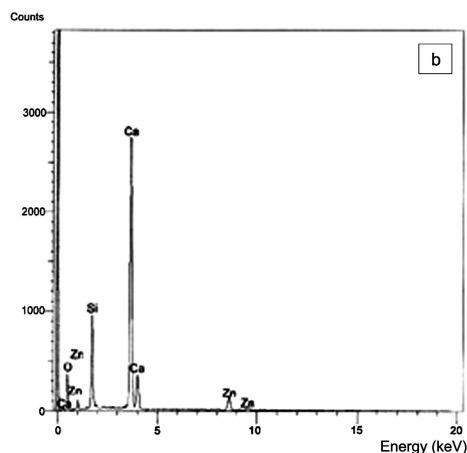
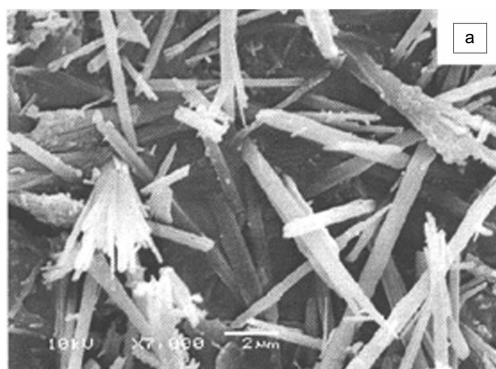


Fig. 10. (a) SEM of $\beta\text{-C}_2\text{SH}$ reacted with 1000 ppm Zn^{2+} solution for 24 h; (b) EDAX of $\beta\text{-C}_2\text{SH}$ reacted with 1000 ppm Zn^{2+} for 24 h.

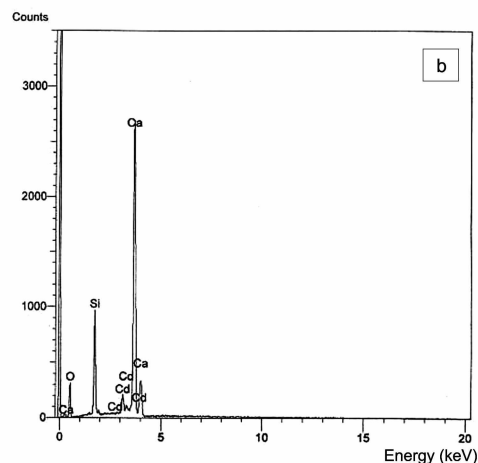
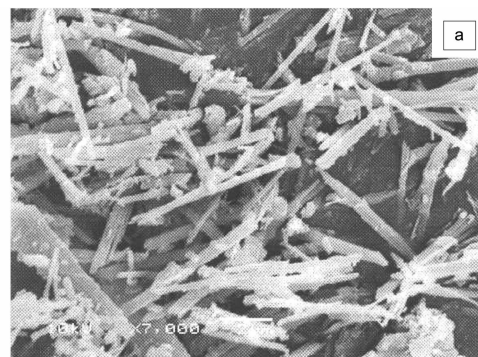


Fig. 11. (a) SEM of $\beta\text{-C}_2\text{SH}$ reacted with 1000 ppm Cd^{2+} solution for 24 h; (b) EDAX of $\beta\text{-C}_2\text{SH}$ reacted with 1000 ppm Cd^{2+} for 24 h.

detected by SEM with EDAX, Fig. 10 a & b), requires a relatively basic medium. This is achieved by the liberation of hydrated Ca^{2+} from the lattice structure of the solid (due to $\text{Ca}^{2+} \leftrightarrow \text{M}^{2+}$), thus elevating the pH values (Table 3).

The reaction of the above mentioned cations with $\beta\text{-C}_2\text{SH}$ leads to a partial loss of crystallinity as can be deduced from the decrease of the relative intensities of d-spacing with respect to the reference (Fig. 1) and the results of microstructures are presented in Fig. 10b and 11b. The most intense FTIR absorption bands of $\beta\text{-C}_2\text{SH}$ (Fig. 12), slightly decrease, especially those located at 1077, 1030, 945, 901 and 454 cm^{-1} upon reaction with Cd^{2+} . The positions of some these are slightly shifted, may be attributed to some modification in the structure, due to $\text{Ca}^{2+} \leftrightarrow \text{Cd}^{2+}$ exchange. Presence of very

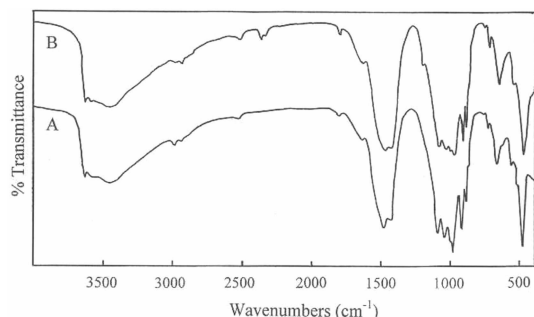


Fig. 12. FTIR spectra of synthesized β -C₂SH (a) and β -C₂SH reacted with 1000 ppm Cd²⁺ (b) for 24 h.

weak sharp band at about 3618 cm⁻¹ confirms the presence of OH⁻ groups which are bound in the structure; while the presence of broad band located at 3445 and weak one at 1630 cm⁻¹ may due to the physically adsorbed water.

Scanning electron microscopy (SEM) results of β -C₂SH reacted with 1000 ppm Zn²⁺ and Cd²⁺ solutions for 24h (Fig. 10a and 11a) support the XRD and FTIR data. They also show that the crystallinity does not completely remain intact upon exchange, especially in the case of Cd²⁺ (Fig. 10a).

The energy dispersive analysis X-ray (EDAX) data of the above samples are given in Figs. (10b & 11b). Fig. 10(b) demonstrates the existence of K_α radiation of Ca, Si and Zn²⁺, while 11(b) demonstrates the existence of K_α radiation of Ca, Si and Cd²⁺. This supports the release of some of the total Ca²⁺ ions present in the crystal structure of β -C₂SH due to exchange with Zn²⁺ or Cd²⁺.

In conclusion, beta-dicalcium silicate hydrate prepared under hydrothermal conditions at Ca/Si=2 (molar ratio) exhibits selectivity for cesium and this selectivity increases in different cations solutions of alkali metals and alkaline metals as follows: Mg²⁺>Li⁺>Ca²⁺>Na⁺≈Ba²⁺>K⁺. The selectivity of the Cs⁺ depends on the hydration status of the present cation in solution. It can be used in partitioning of radioactive Cs⁺ from nuclear wastes containing numerous cations. The β -C₂SH has a cation exchange capacity equal to 0.287 meq/g, so it can be used as cation exchanger for the separation of heavy metals

from the hazardous waste stream. The amount of removal of heavy metal ion by β -C₂SH increases in the order: Fe²⁺>Cu²⁺>Zn²⁺>Cd²⁺≈Pb²⁺. The total cations uptake is appeared to be due to both exchange of Ca²⁺ ↔ M²⁺ and immobilization (precipitation) of M²⁺ as salts.

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