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Synthetic Crystalline Calcium Silicate Hydrate (I): Cation Exchange and Caesium Selectivity

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Summary. Solid crystalline calcium silicate hydrate (I) synthesized from equimolar amounts of Ca and Si under hydrothermal conditions at 120°C shows cation exchange properties towards divalent metal cations such as Ni, Cu, Cd, or Hg. It also exhibits caesium selectivity in the presence of Na^+. The exchange capacity and selectivity of the solid can be increased by 10 and 28%, respectively, upon substitution of 0.01 mol of the Ca^{2+} in its structure by Na^+. The ability of metal cation uptake by the solid was found to obey the order $Ni^{2+} > Hg^{2+} > Cu^{2+} > Cd^{2+}$. The different affinities of calcium silicate hydrate (I) towards these ions can be used for their separation from solutions and also in nuclear waste treatment. The mechanism of the exchange reaction is discussed.

Keywords. Calcium silicate hydrate (I); Transition metals; Mechanism of exchange reaction; Caesium selectivity.

Introduction

Many crystalline calcium silicate hydrate compounds are known. Most of them are formed under hydrothermal conditions, *i.e.* in aqueous systems under elevated pressure above 100°C. Two representatives can be prepared in aqueous suspension below 100°C: 1.1-*nm*-tobermorite ($5CaO \cdot 6SiO_2 \cdot 5H_2O$) and jennite ($9CaO \cdot 6SiO_2 \cdot H_2O$). Various types of semicrystalline calcium silicate hydrates are intermediate in structure between these compounds and calcium silicate hydrate gel. Two relatively well defined ones are $CaO \cdot SiO_2 \cdot H_2O$(I) and $CaO \cdot SiO \cdot H_2O$(II) which are closely related to 1.4-*nm*-tobermorite and jennite, respectively [1].

Calcium silicate hydrate (I) (*CSH*(I); C=CaO, S=SiO_2, H=H_2O) has been obtained by decomposition of C_3S with water at unspecified solids ratio and temperature. A similar compound, also denoted as *CSH*(I), has been prepared by hydrothermal reaction of CaO/SiO_2 mixtures in molar ratios of Ca:Si = 1:1 or 3:2 [2].

CSH(I) is similar in structure to 1.4-*nm*-tobermorite and jennite, and its average layer structure consists of two-dimensional distorted Ca–O sheets with Si–O chains. All oxygen atoms in the 'CaO_2' lattice structure are shared with Si–O chains which

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form ribs covering each surface. Between its layers, H_2O molecules and additional Ca atoms are located. The OH^- groups in *SCH*(I) are attached to both end groups in a tetrahedral way as deduced from ^{29}Si NMR measurements [3]. The compound exhibits relatively sharp reflections at 0.304 nm and 0.183 nm (interlayer distance) which correspond to the (220) and (040) spacing of crystalline 1.1-*nm*-tobermorite as demonstrated by X-ray diffraction studies.

Many types of inorganic materials act as cation exchangers (layered zirconium phosphate, clay minerals, hydroxyapatities, frame work alumosilicates, *etc.*). These substances have been recognized for their potential application due to low cost of synthesis and remarkable ion selective properties towards a large number of metal cations from their solutions. Applications include water softening, catalysis, fertilizer production, or fixing of hazardous isotopes in cement and concrete materials [4–7]. Some authors have reported that a series of *CSH* compounds, mainly 1.1-*nm*-tobermorite, 1.1-*nm*-ion substituted tobermorite, and xonotlite, act as cation exchangers with Ca^{2+} or Si^{4+} in their lattice structure [8–16].

The objectives of this paper are to show the exchange properties and ^{137}Cs selectivity of crystalline calcium silicate hydrate (I) synthesized under mild hydrothermal conditions in order to fully realize its potential in hazardous waste stream and nuclear waste treatment.

Results and Discussion

Powder XRD analysis (Fig. 1) showed that one single phase of *CSH*(I) agreed with ASTM card No. 9-210. This phase consisted of a crumpled foil of crystals when examined by SEM (Fig. 2a). EDAX measurements (Fig. 2b) prove the existence of K_α radiation of Ca and Si; the results are in good agreement with data obtained by chemical analysis (Table 1). Solid *CSH*(I) can incorporate 10 meq of Na^+ ions per 100 g in its crystal lattice upon treatment with 1 *N* NaCl. This amount is available for exchange with metal cations. Table 1 also shows the cation exchange capacity (*CEC*) and caesium selectivity for *CSH*(I) and Na–*CSH*(I); the changes in *pH* value upon the reaction are given in Table 2.

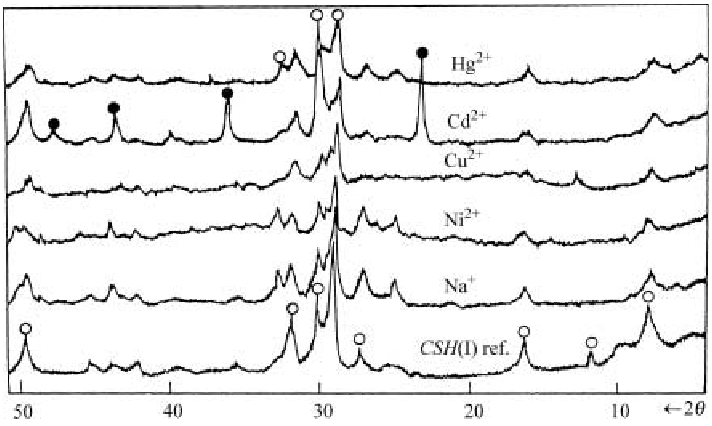

Fig. 1. XRD patterns of *CSH*(I) reacted with 1 *N* NaCl and 1000 ppm of Ni^{2+}, Cu^{2+}, Cd^{2+}, or Hg^{2+} for 24 h (○: *CSH*(I), ●: $CdCO_3$)

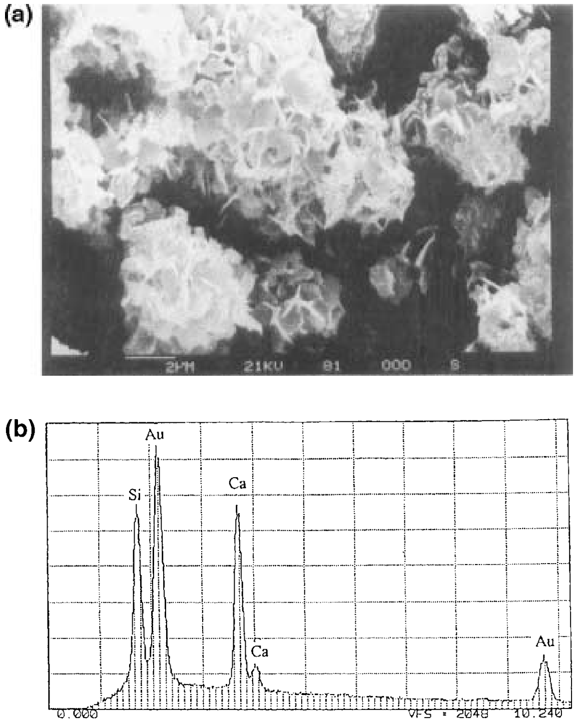

Fig. 2. (a) SEM of synthesized *CSH*(I) crystals; (b) EDAX of *CSH*(I)

Table 1. Chemical composition, cation exchange capacity (*CEC*), caesium selectivity, and K_d for *CSH*(I) and Na–*CSH*(I)

Solid	Chemical composition	*CEC* (meq/100 g)	Cs selectivity (meq/100 g)	K_d
CSH(I)	$CaO \cdot SiO_2 \cdot 0.98H_2O$	17.4	3.75	7.54
Na–*CSH*(I)	$CaO_{0.99} \cdot NaO_{0.01} \cdot SiO_2 \cdot 1.01H_2O$	19.45	4.81	6395.00

An examination of the data in Table 1 shows that Na–*CSH*(I) is superior to *CSH*(I) with respect to the properties discussed above. This may be attributed to the fact that Na^+ is less hydrated than Ca^{2+} and can hence easily be substituted. This leads to the result that 10 meq of Na^+ in 100 g of solid *CSH*(I) improve the *CEC* potential and caesium selectivity by 10 and 28%, respectively.

The X-ray intensities of (002), (220), and (040) spacings at $2\theta = 7.7$, 29, and 49.65°, respectively, decrease upon treatment of solid *CSH*(I) by 1 *N* NaCl (Fig. 1), indicating that the Na^+ ions are incorporated *via* an ion exchange process ($2Na^+ \rightleftharpoons Ca^{2+}$) and not absorbed on the surface.

Results of the exchange reaction of Ni^{2+}, Cu^{2+}, Cd^{2+}, or Hg^{2+} with Ca^{2+} in *CSH*(I) are presented in Figs. 3 and 4, whereas the of the reaction of Cd^{2+} with Na–*CSH*(I) can be found in Table 3. In these reactions, the $M^{2+} \rightleftharpoons Ca^{2+}$ interchange almost reaches the stoichiometric values, except in the case of Hg^{2+} (the reason will be discussed later). The amount of Cd^{2+} exchanged with Ca^{2+} in Na–*CSH*(I) is higher than in *CSH*(I) (Fig. 4, Table 3). Generally, the amount of metal ions taken up

Table 2. *pH* values of reacted metal solutions

$[M^{2+}]$/ppm	Reaction time (h)	Ni^{2+}	Cu^{2+}	Cd^{2+}	$Cd^{2+\,a}$	Hg^{2+}
200	0	6.36	5.65	6.38	6.38	2.66
400		6.59	5.54	6.32	6.32	2.21
800		6.70	5.33	6.30	6.30	2.02
1000		6.68	5.23	6.15	6.15	1.95
200	1	7.51	5.69	6.20	6.52	7.12
400		7.18	5.85	6.46	6.46	7.18
800		7.05	5.34	6.16	6.16	3.73
1000		7.04	5.25	6.15	6.14	3.32
200	6	7.41	6.15	6.68	7.38	7.21
400		7.60	5.92	6.45	6.46	7.99
800		7.19	5.42	6.38	6.33	5.82
1000		7.02	5.32	6.50	6.19	3.73
200	12	8.26	6.63	7.31	7.34	7.28
400		7.73	5.93	6.53	6.84	7.64
800		7.36	5.27	6.38	6.36	7.03
1000		7.25	5.55	6.36	6.25	3.86
200	24	7.53	7.75	7.17	6.89	7.39
400		7.63	5.81	6.71	6.28	7.55
800		7.42	5.40	6.76	7.57	6.16
1000		7.45	5.46	5.58	6.35	6.18

[a] Reacted with Na–*CSH*(I)

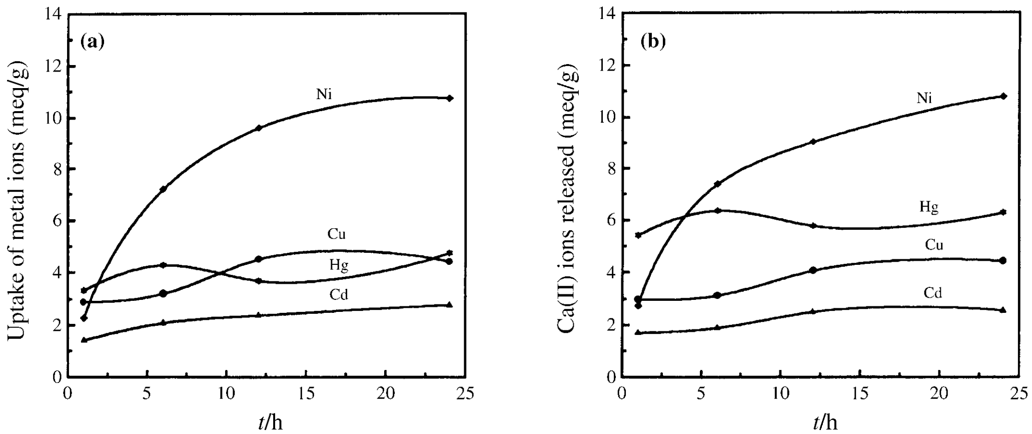

Fig. 3. Uptake of metal ions from 1000 ppm aqueous solution (a) and amount of Ca^{2+} released (b) from *CSH*(I)

by *CSH*(I) increases with increasing reaction time and/or initial M^{2+} concentration in the order $Ni^{2+} > Hg^{2+} > Cu^{2+} > Cd^{2+}$. The non-stoichiometricity in case of Hg^{2+} are attributed to the acidic nature of the initial solutions (Table 2) and the basic nature of *CSH*(I) and/or Na–*CSH*(I). In addition, precipitation of some cations as *e.g.* Cd^{2+} in the form $CdCO_3$ has been detected by XRD (Fig. 1). This means that limited

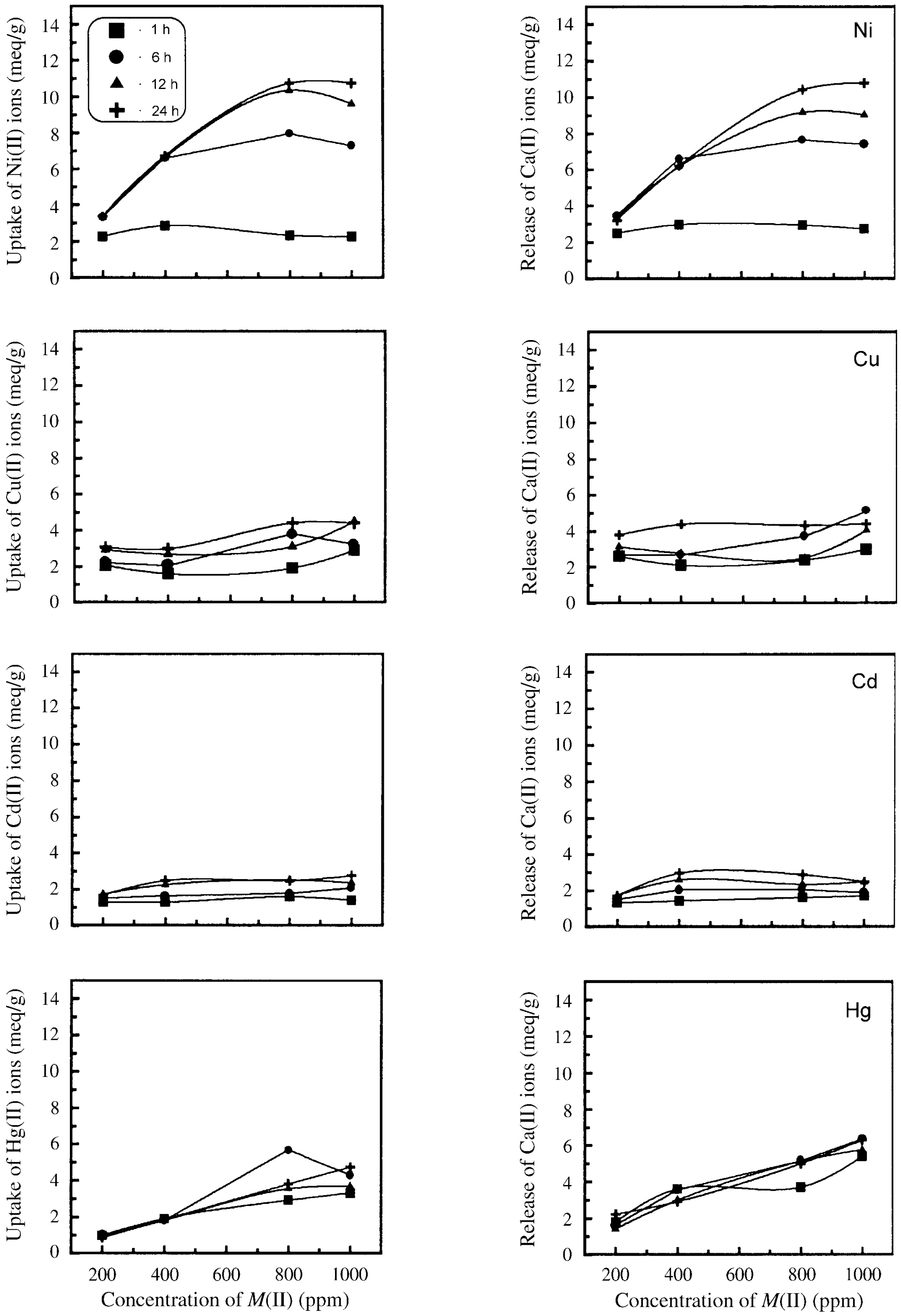

Fig. 4. Effect of concentration and time on M(II) uptake and Ca(II) release from *CSH*(I)

Table 3. Concentrations of Cd^{2+} taken up and Ca^{2+} released by Na–*CSH*(I)

$[M^{2+}]$/ppm	Reaction time (h)	Cd^{2+} uptake (meq/g)	Ca^{2+} release (meq/g)	Wt. of Cd^{2+} uptaken	Wt. of Ca^{2+} released	Cd^{2+}/Ca^{2+} (molar ratio)
200	1	1.335	1.392	75.025	6.662	0.959
400		1.421	1.431	39.930	6.848	0.993
800		0.916	1.484	12.869	7.102	0.617
1000		0.876	1.250	9.846	5.982	0.700
200	6	1.759	1.624	98.854	7.772	1.083
400		2.801	2.313	78.709	11.069	1.210
800		2.749	2.567	38.624	12.285	1.070
1000		2.763	2.695	31.056	12.897	1.025
200	12	1.776	1.563	99.809	7.480	1.136
400		3.171	2.902	89.106	13.888	1.092
800		3.176	2.843	44.623	13.606	1.117
1000		2.879	2.617	32.360	12.524	1.100
200	24	1.762	2.077	96.999	9.939	0.848
400		3.279	2.891	92.140	13.836	1.134
800		3.736	3.148	52.491	15.065	1.186
1000		3.337	3.266	37.508	15.630	1.021

partial hydrolysis of silicate chains of the solid may take place; accordingly, extra Ca^{2+} ions were detected in solution, which also may be responsible for the non-stoichiometric data.

The exchange reaction in *CSH*(I) may take place from edge and planar surface sites as well as from the interlayer Ca^{2+} sites due to its structural similarity to 1.4-*nm*-tobermorite [1, 16, 19]. Since all oxygen atoms are shared with Si–O chains in the central sheet structure of 'CaO_2' (its average layer structure consists of two-dimensional distorted Ca–O sheets) in *CSH*(I), the Ca–O interaction will became weaker (Fig. 5). In some cases, the ratio of metal ions taken up by the solid is greater than the *CEC* of *CSH*(I) or Na–*CSH*(I) (Table 1). This is considered to be

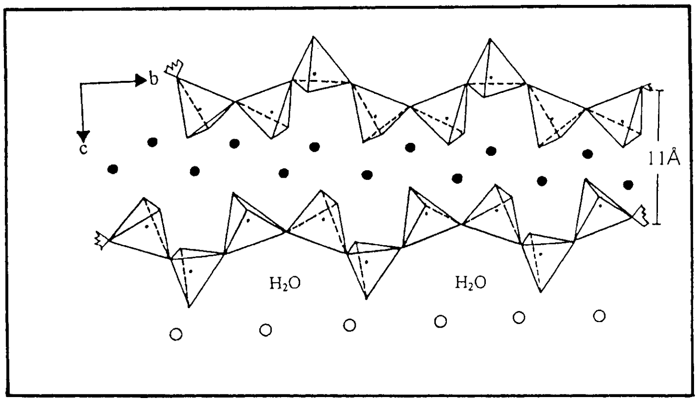

Fig. 5. Two-dimensional distorted Ca–O sheet with Si–O chain structure of *CSH*(I) (•: silicon, ●: structural calcium, ○: interlayer calcium)

due to the precipitation of Cd^{2+} as its carbonates during the reaction. This means that the reaction of *CSH*(I) with Ni^{2+}, Cu^{2+}, and/or Hg^{2+} is mainly due to an exchange of the type $Ca^{2+} \rightleftharpoons M^{2+}$, whereas in case of Cd^{2+} a mixed effect between partial exchange and immobilization (precipitation) is operative. The maximum amount of Ca^{2+} released from solid *CSH*(I) has been detected in the case of Hg^{2+} and Ni^{2+}.

The reaction of *CSH*(I) with Cd^{2+} leads to precipitation of otavite ($CdCO_3$) as shown in the corresponding XRD pattern (Fig. 1). Precipitation of this phase requires a relatively basic medium. This is achieved by the liberation of hydrated Ca^{2+} and or Na^{2+} (in the case of Na–*CSH*(I)) from the lattice of the solid, thus elevating the *pH* value.

The reaction of Ni^{2+}, Cu^{2+}, Cd^{2+}, and/or Hg^{2+} leads to a partial loss of crystallinity of *CHS*(I) as can be deduced from the decrease of the relative intensities of d-spacing with respect to the reference (Fig. 1) and the microstructures as shown in Figs. 6a–9a as well as from the infrared spectra (Fig. 10). The most intense IR absorption bands of *CSH*(I) decrease, especially those located at 3600-400, 1630, 1475, 965, 870, 605, and 445 cm^{-1}. The position of some those are slightly shifted, and new less intense bands could be detected; this may be attributed to some modification in the structure in addition to precipitation phenomena.

Scanning electron microscopy (SEM) results of *CSH*(I) reacted with 1000 ppm M^{2+} solutions of the concerned cations for 24 h (Figs. 6a–9a) support the XRD and IR data. They also show that the crystallinity does not completely remain intact upon exchange, especially in the case of Hg^{2+}, Ni^{2+}, and Cu^{2+}. In case of Cd^{2+},

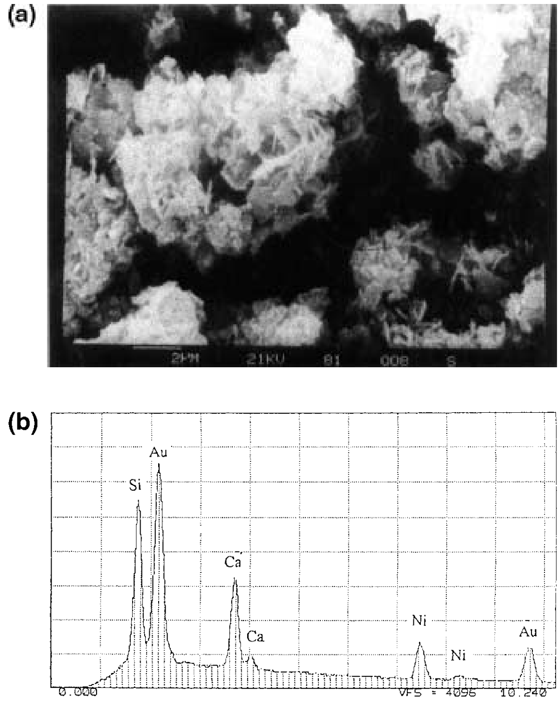

Fig. 6. (a) SEM of *CSH*(I) reacted with 1000 ppm Ni^{2+} solution for 24 h; (b) EDAX of *CSH*(I) reacted with 1000 ppm Ni^{2+} for 24 h

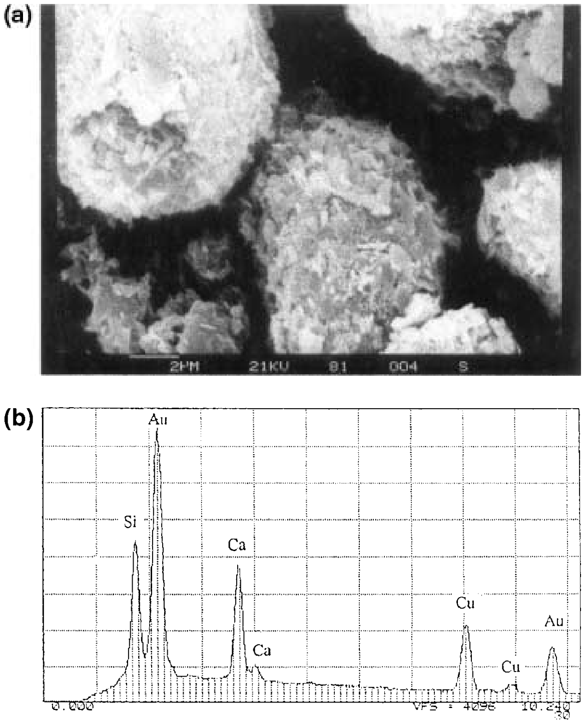

Fig. 7. (a) SEM of *CSH*(I) reacted with 1000 ppm Cu^{2+} solution for 24 h; (b) EDAX of *CSH*(I) reacted with 1000 ppm Cu^{2+} for 24 h

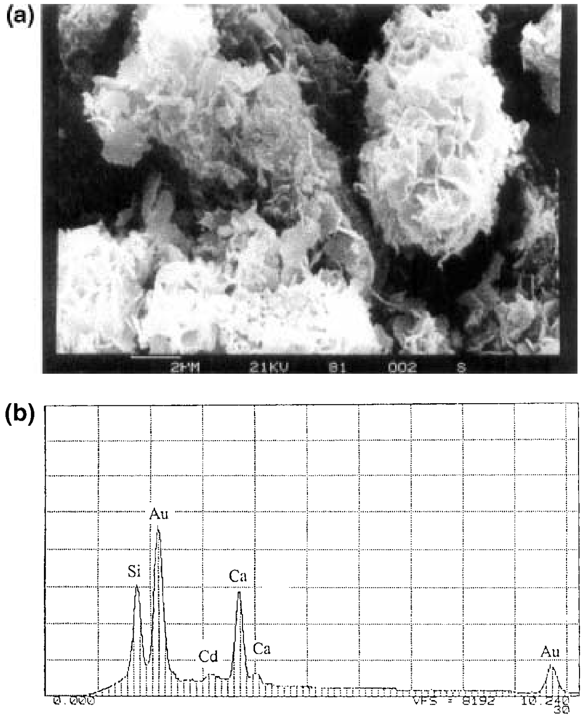

Fig. 8. (a) SEM of *CSH*(I) reacted with 1000 ppm Cd^{2+} solution for 24 h; (b) EDAX of *CSH*(I) reacted with 1000 ppm Cd^{2+} for 24 h

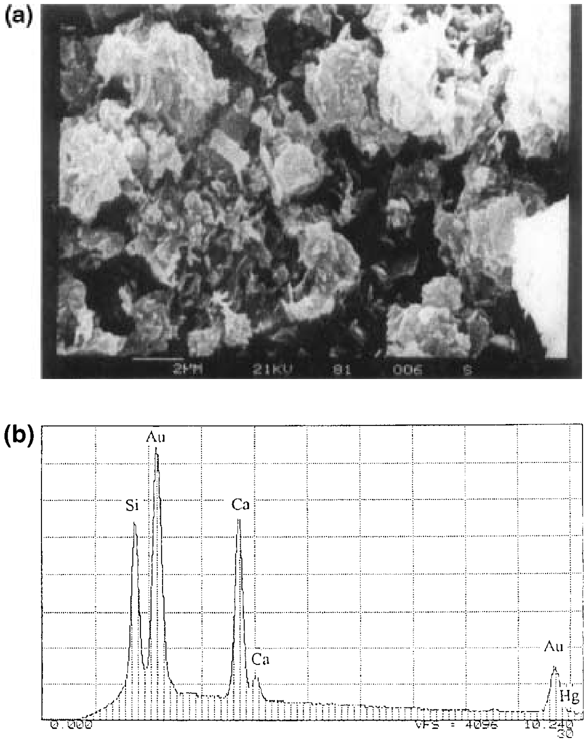

Fig. 9. (a) SEM of *CSH*(I) reacted with 1000 ppm Hg^{2+} solution for 24 h; (b) EDAX of *CSH*(I) reacted with 1000 ppm Hg^{2+} for 24 h

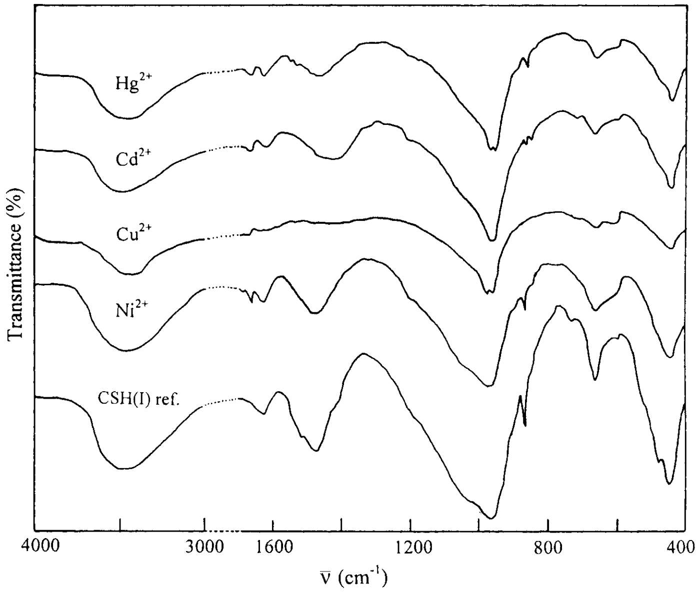

Fig. 10. Change in relative intensities of IR bands of synthetic *CSH*(I) upon reaction with metal ions for 24 h

the crystallinity is only weakly affected (Fig. 7a); instead, tetragonal crystals of $CdCO_3$ are formed on the *CSH*(I) crystals.

The energy dispersive analysis X-ray data (EDAX) of the above samples are given in Figs. 6b–9b. Figure 6b demonstrates the existence of K_α radiation of Ca, Si, and Ni. The detected Ca peak is less intense than the Si peak by about 50% and also less intense than the reference (Fig. 2b). This supports the release of some of the total Ca^{2+} ions present in the crystal lattice of *CSH*(I) due to exchange with Ni^{2+}. In this respect, *Komarneni et al.* [9] have shown by TEM and EDS that Ni^{2+} could be detected at the edge but not at the core upon reaction of tobermorite with Ni^{2+} (uptake of 2.7 meq Ni^{2+}/g). Their results indicate that the mechanism of reaction takes place from edge to core and the partial replacement leads to amorphization of the crystals in the rim only, whereas almost complete replacement leads to total amorphization. Appearance of Ni, Cu, Cd, and Hg peaks in the EDAX diagrams (Figs. 6b–9b) confirm the presence of these ions due to $Ca^{2+} \rightleftharpoons M^{2+}$ exchange.

In conclusion, calcium silicate hydrate (I) prepared under mild hydrothermal conditions can be used as cation exchanger for the separation of heavy metals from the hazardous waste stream and as caesium selective reagents for nuclear waste treatment. The amount of removal of heavy metal ions by *CSH*(I) decreases in the order $Ni^{2+} > Hg^{2+} > Cu^{2+} > Cd^{2+}$. Its exchange capacity and selectivity can be increased by treatment of the solid by 1 *N* NaCl due to the incorporation of some of less hydrated Na^+ ions in its crystal structure. Although zeolites and clay minerals can be used for Cs separation from radioactive waste solutions, solid *CSH*(I) and/or Na–*CSH*(I) are well suited not only for Cs separation but also for subsequent immobilization in cement or in concrete materials because they are thermodynamically stable in cement environment. *CSH*(I) is the main hydration reaction product of cements, whereas zeolites and clays are not.

Experimental

Solid calcium silicate hydrate (I) was synthesized by mixing stoichiometric amounts of CaO and SiO_2 (silica fume below 11 μ) at a molar ratio equal to one. CaO was prepared by ignition of British Drugs House (BDH) grade of $CaCO_3$ at 1050°C for 3 h. The solid was added to 20 times of its weight of decarbonated deionized water and stirred for 10 min in 250 cm^3 beaker. 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 120°C and kept at this temperature for 48 h. At the end of the run the autoclave was cooled, and the content was washed with few cm^3 of distilled water and dried at 60°C for 24 h. The solid was characterized by X-ray powder diffraction (Philips diffractometer using Ni filtered CuK_α radiation), SEM, EDAX, IR spectroscopy, and chemical analysis.

Na substituted *CSH*(I) was prepared by treatment of a defined weight of solid *CSH*(I) with 1 *N* NaCl solution for 24 h without stirring. Then the solid was filtered off, washed three times with deionized water, and dried at 60°C for 24 h. This step was carried out to show the effect of $2Na^+ \rightleftharpoons Ca^{2+}$ substitution on the exchange capacity and the selectivity potential.

The cation exchange capacity (*CEC*) of *CSH*(I) and Na–*CSH*(I) were measured using a known method [17] as follows: 20 mg of each solid was repeatedly washed with 0.1 *N* KCl to saturate all exchange sites with K^+, followed by removing excess KCl with 0.01 *N* KCl to prevent any hydrolysis (a correction was made for excess 0.01 *N* KCl which was determined by weighing), and displacing

K^+ from the exchange sites with four washing (30 min equilibrium time per washing) of 1 *N* CsCl. The displaced K^+ was determined by atomic emission spectroscopy (AES).

Caesium selectivity was tested using a method reported by *Komarneni et al.* [18]. Briefly, the method proceeds by addition of 10 cm^3 of 0.02 *N* NaCl containing 0.0002 *N* CsCl to 20 mg of each solid, equilibrating for 1 day in glass vials, centrifuging to separate phases, and analyzing Cs^+ by atomic absorption spectroscopy (AAS). Cs^+ adsorption is expressed as K_d (in cm^3/g; K_d is a distribution coefficient defined as the ratio of the amount of caesium adsorbed per gram of solid to the amount of Cs^+ remaining per cm^3 of solution).

Cation exchange reaction experiments were conducted as follows: 20 mg of each solid were equilibrated for different periods in glass vials with 20 cm^3 of Cl^- or NO_3^- solution of 200, 400, 800 or 1000 mg/dm^3 of Ni^{2+}, Cu^{2+}, Cd^{2+} or Hg^{2+}; NO_3^- was used for Hg^{2+}. After different periods of equilibration (1–24 h) 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 AAS. Na–*CSH*(I) was used in case of Cd^{2+} only. The *pH* of the equilibrium solutions for reaction in the glass vials was immediately measured. The samples were then dried at 60°C in an oven prior to characterization by XRD, SEM (Cambridge Stereoscan 250 MK 30 high resolution SEM with energy dispersive analysis) X-ray (EDAX), and IR spectroscopy.

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