Articles

Cation Exchange of Alkali Metal Hydroxides with Some Hydrothermally Synthesized Calcium Silicate Compounds

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Abstract

Crystalline calcium silicate hydrate compounds: xonotlite ($6\text{CaO} \cdot 6\text{SiO}_2 \cdot \text{H}_2\text{O}$) and gyrolite ($4\text{CaO} \cdot 6\text{SiO}_2 \cdot 3\text{H}_2\text{O}$) synthesized at CaO/SiO_2 mole ratios of 0.67 and 1.0 under hydrothermal conditions show cation exchange capacities amounting to 41.70 and 44.40 meq/100 g respectively. They also exhibit cation exchange properties toward alkali-metal ions such as Na^+ and K^+ as hydroxides (MOH) with concentrations ranging from 0.005–0.10 mol/l. The uptake of M^+ by the gyrolite solid was found to be larger than xonotlite. It also increases with the increase of MOH concentrations and/or the time of reaction. This uptake was reached the equilibrium after 24 hrs, and the amount of K^+ -ions entered into the crystal structure of the solids (mmol/100 g) was found to be larger than Na^+ -ions. The equilibrium amounts of alkali-metal ions incorporated into the mentioned solids (mmol/100 g) were found to be 40.96 for K^+ and 39.97 for Na^+ with gyrolite, 37.44 for K^+ and 36.74 for Na^+ with xonotlite at 0.1 M MOH after 24 hrs. The $\text{Ca}^{2+} \rightleftharpoons \text{M}^+$ ratio ($\text{M}^+/\text{Ca}^{2+}$) was found to be 1 at concentrations up to 0.025 mol/l MOH with a slight decrease of a value smaller than 1 at higher concentrations. The affinities of xonotlite and gyrolite for alkali metal ions can be used for their separation from solutions. The mechanism of the exchange reaction is discussed.

Keywords: calcium silicate hydrate; alkali metal hydroxides; cation exchange.

1. Introduction

There is a large number of crystalline calcium silicate hydrate compounds in the $\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$ system as summarized by Taylor¹⁾. Most of them are synthesized under hydrothermal reaction conditions, i.e., in aqueous systems under elevated pressure with temperatures above 100°C. The tobermorite group and the compounds structurally related to the wollastonite ($\text{CaO} \cdot \text{SiO}_2$) such as nekoite, okenite, xonotlite, gyrolite, etc. are very technically important crystalline calcium silicates. The advantage of these silicates is that they are of very low cost of preparation, and have layer structures. Recently they have been recognized as a new family of cation exchangers for the removal of a heavy metals from waste waters and in nuclear waste treatment and disposal, in addition they have ion selective properties. They can also be used as thermal

insulating materials, fire-resistance coating materials, catalyst support and filler in deep oil or geothermal wells besides in ethylene adsorptivity, flue gas desulfurization and antibacterial activity. Xonotlite and gyrolite are natural hydrous calcium silicate compounds with layer structure like clay minerals. They are considered to be very stable calcium silicate compounds and to be prepared hydrothermally above 200°C.

Various types of inorganic materials act as cation exchangers (clay minerals, hydroxyapatites, layered zirconium phosphate, frame work aluminosilicates, etc.). 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 solutions. The applications include water softening, catalysis, fertilizer production or fixing of

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hazardous isotopes in various materials²⁻⁷). Certain calcium silicate hydrate compounds prepared by hydrothermal treatment acting as cation exchangers can exchange divalent cations releasing Ca^{2+} and/or $\text{Si} (+\text{IV})$ ^{4,8-19} leading to their amorphization^{4,15,16}). Also they can select cesium during nuclear waste treatment^{19,20}).

Na^+ -ions (from NaOH) accelerates the hydrothermal synthesis of calcium silicates in the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2-\text{H}_2\text{O}$, and it incorporates in the CSH ($\text{C}=\text{CaO}$, $\text{S}=\text{SiO}_2$, $\text{H}=\text{H}_2\text{O}$) or tobermorite structure²¹⁻²³). The reaction of alkali metal hydroxides (Li, Na, and/or K) with synthetic 11.3 Å-tobermorite ($\text{Ca}_5\text{Si}_6\text{H}_2\text{O}_{18}\cdot 4\text{H}_2\text{O}$) was studied¹³). The results obtained indicated that this reaction highly depends on the pH of MOH solution in addition to the relative activity of the cation and to a lesser degree on the ionic radius of M.

The objectives of the present paper are to show the cation exchange capacity and properties of very low cost and remarkably stable crystalline calcium silicate compounds, in particular xonotlite and gyrolite towards Na and K. In order to fully understand the potentialities of these exchangers in cation separation from aqueous alkaline solutions. The mechanism of the metal cations exchange by the present exchangers solids is discussed.

2. Experiment and methods

2.1 Synthesis of the solid

Calcium silicate hydrate solids of xonotlite and gyrolite were synthesized by mixing stoichiometric amounts of CaO and SiO_2 at a mole ratio of 1.0 and 0.67 respectively. Alpha quartz (99.73% SiO_2 purity) with grain size less than 45 mm was used in xonotlite, while silica fume (silica content 99.8%) with particle size below 0.008 mm and the specific surface area of $325 \pm 25 \text{ m}^2/\text{g}$ (supplied by Sigma Chemical Co.) was used for the case of hydrothermal synthesis of gyrolite. CaO was prepared by ignition of CaCO_3 (British Drugs House grade) at 1050°C for 3 h. Each solid mixture was added to 20 times larger weight of decarbonated deionized water and stirred for 15 min in a 250 cm^3 beaker. The content of each of them was quantitatively transferred to a stainless steel autoclave bomb (250 cm^3) internally coated with Teflon. Each autoclave was placed in a manually controlled electrically heated oven. The temperature was raised gradually to 200°C and kept at this degree for 7 days in the synthesis of xonotlite solid, while at 220°C for 7 days in the synthesis of gyrolite solid. At the end of each run the autoclave was cooled, and the content was washed with a few cm^3 of distilled water and dried at 60°C for 24 hrs.

2.2 Cation Exchange Capacity (CEC) of the solids

The CEC (meq/100 g) of xonotlite and gyrolite solids was determined by using the method reported previously¹⁶). 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 10 ml of 0.1 M KCl solution to saturate all the exchange sites with K^+ , followed by washings with 0.02 M KCl five times (10 ml) 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 0.2 M CsCl four times. The solution was collected and analyzed for K^+ by Atomic Emission Spectroscopy (AES) and the total CEC was determined.

2.3 Cation exchange reaction experiments

Cation exchange reaction of MOH with the solids was conducted as follows: 25 mg of each solid was equilibrated for different periods (1–24 h) in closed polyethylene vials with 10 ml of NaOH and/or KOH (analytical grade) solutions of 0.005–0.10 mol/l. After different periods of equilibrium, the solid phases in the vials were separated by centrifugation, and a part of the supernatant solution was collected for chemical analysis using atomic emission spectroscopy (AES) for Na^+ and/or K^+ and atomic absorption spectroscopy (AAS) for Ca^{2+} -ions released from the solids. The pH of the equilibrium solutions for each reaction were immediately measured using digital pH-meter (Fisher Scientific, Model 825 MP) with combined glass electrode equipped with Ag/AgCl reference electrode.

2.4 Characterization of the solids

The xonotlite and gyrolite exchangers before and after exchange process were dried at 60°C in an oven for 24 hrs and characterized by X-ray powder diffraction (XRD) (Philips diffractometer using Ni filtered Cu K_α radiation). A JEOL scanning electron microscope JSM-5600 attached with an energy dispersive X-ray (EDAX) (ISIS OXFORD) source was used for determining the microstructure and chemical composition.

3. Results and Discussion

Powder XRD analysis of the synthesized solids showed that one single phase in both of xonotlite (**Fig. 1**) and gyrolite (**Fig. 2**) was obtained. This agrees at ASTM card number's 3-0568 and 12-217, respectively. Microstructure of xonotlite composed of aggregates of long fibrous crystals (**Fig. 3a**), while flower-like aggregate crystals were found in the case of gyrolite (**Fig. 4a**) as examined by scanning electron microscope (SEM). EDAX measurements (**Figs. 3b** and **4b**) prove the existence of Ca and Si due to the K_α

Fig. 1 XRD patterns of synthesized xonotlite reacted with 0.1 M NaOH and 0.1 M KOH for 24 h.

Fig. 2 XRD patterns of synthesized gyrolite reacted with 0.1 M NaOH and 0.1 M KOH for 24 h.

Table 1 Chemical composition and cation exchange capacity (CEC) of the solids prepared under hydrothermal treatment

Solid	Chemical composition	CEC (meq/100 g)
Xonotlite	$\text{Ca}_{6.09}\text{Si}_{5.92}\text{O}_{16.96}(\text{OH})_2$	41.70
Gyrolite	$\text{Ca}_{3.98}\text{Si}_{6.02}\text{O}_{15}(\text{OH})_2 \cdot 3.02\text{H}_2\text{O}$	44.40

radiation of these elements for xonotite and gyrolite respectively.

Table 1 shows the chemical composition of synthesized products and their cation exchange capacity (CEC). The total value of CEC of xonotlite and gyrolite which based on displaced K^+ is 41.7 and 44.4 meq/100 g respectively, and they represent the extent of reversible exchange reaction.

The changes of the pH-values as well as those of electrical conductivity of the reacted MOH solution are presented in **Tables 2** and **3**, respectively. The amounts of Na^+ and K^+ species incorporated into the solids and the released Ca^{2+} -ions from the silicates structure at different MOH concentrations and their calculated $\text{M}^+/\text{Ca}^{2+}$ ($\text{M}^+ = \text{Na}^+$ or K^+) mole ratios are given in **Tables 4** and **5**. The increase of pH-values of MOH solutions with increase of the

Fig. 3 (a) SEM of xonotlite reacted with 0.1 M NaOH for 24 h; (b) EDAX of xonotlite reacted with 0.1 M NaOH for 24 h.

reaction time are due to the increase of incorporated M^+ in the lattice structure of the concerned solids that exchanged with Ca^{2+} -ions. The pH and electrical conductivity measurements (**Table 2**) indicate that K^+ -ions are more preferred to enter in the lattice structure of the solids than Na^+ -ions. This may be due to the fact that K^+ -ions has a hydrated ionic radius less than the corresponding Na^+ -ions, in addition to the increase of relative activity of K^+ compared with Na^+ .

In general, the increase of pH-values as a result of solid-MOH reactions may be achieved from the exchange of one mole of a divalent Ca^{2+} ion with one mole of monovalent (Na^+ and/or K^+) ion (**Tables 4** and **5**). Charge balance equilibrium can be realized by one of the following: First, $\text{Ca}^{2+} \rightleftharpoons \text{M}^+ + \text{H}^+$ (from solution) second from an extra monovalent negative ions (e.g. OH^-) released, since part of H_2O molecules as hydroxyl (OH -group) are bounded in their silicate lattice structures. The presence of OH^- groups was confirmed by the presence of two strong absorption bands at 3613 and 3637 cm^{-1} in FTIR spectra of

Fig. 4 (a) SEM of gyrolite reacted with 0.1 M KOH for 24 h; (b) EDAX of gyrolite reacted with 0.1 M KOH for 24 h.

Fig. 5 Kinetics of Na⁺ and K⁺ uptake by xonotlite (a) and gyrolite (b) from 0.1 M MOH.

xonotlite and gyrolite compounds, respectively, and absorption bands around 1200 cm^{-1} due to its bending frequency²⁷⁾. In addition, release of Ca^{2+} from lattice/solution system result in the formation of hydrated Ca^{2+} which contributes in increasing pH-values via the change of ionic strength of the solutions¹⁴⁾.

Tables 4 and 5 clearly demonstrate the increase of Ca^{2+} -ions released with increasing alkali metals concentrations and reaction equilibrium time. The $\text{M}^+ \leftrightarrow \text{Ca}^{2+}$ exchange is near the stoichiometric value 1 in most cases, especially in diluted concentrations of MOH. Only at concentrations higher than $2.5 \times 10^{-2}\text{ mol/l}$ of MOH the amounts (mmol/g) of Ca^{2+} -ions released from the solids were higher than the corresponding Na⁺ and/or K⁺ uptaken (**Tables 4 and 5**). This may be attributed to the presence of extra Ca^{2+} in solutions at concentrations above $2.5 \times 10^{-2}\text{ mol/l}$ MOH. This behavior resulted from the presence of limited partial hydrolysis (cleavage) of some Si–O–Si bond of SiO_4 tetrahedral structure of xonotlite (**Fig. 6a and b**) and/or in gyrolite (**Fig. 7**); and this may facilitate the exchange of M^+

with the interlayer Ca^{2+} . This hydrolysis was confirmed by detection of some mmol/g of Si(+IV) in solutions from 0.0104–0.047 mmol/g, by using molybdenum blue photometric-method¹³⁾. In this respect, it was reported^{14,16)} that the reaction of Mg^{2+} and/or MOH with 11.3 Å-tobermorite, Si(+IV)-ions released from its lattice structure at higher concentrations of Mg^{2+} and/or MOH solutions. This was attributed to the cleavage of some Si–O–Si bonds in the solid. Since all oxygen atoms shared with Si–O chains ion the central sheet of CaO_2 (peroxide chain) in the solid, the Ca–O interaction will become weaker and this contributes for extra Ca^{2+} -ions release in solution. H. Stade²⁴⁾ found that the amount of the incorporated MOH increases with the decrease of CaO/SiO_2 mole ratio of synthesized calcium silicates hydrate. This conclusion agreed at data reported in **Tables 4 and 5** as long as the CaO/SiO_2 molar ratio in gyrolite (0.67) is smaller than xonotlite (1.0). The uptake of MOH was assumed to take place most probably by a reaction of the hydroxide with SiOH groups at the in-

Table 2 Change in pH-value of alkali metals hydroxides on reaction with solids

Solid	Concn. of alkali (mol/l)	Alkali metal hydroxide									
		NaOH					KOH				
		Initial pH	pH eq. at different reaction time/h				Initial pH	pH eq. at different reaction time/h			
			1	6	12	24		1	6	12	24
Xonotlite	5×10^{-3}	11.66	11.69	11.77	11.91	11.98	11.71	11.78	11.83	11.89	11.94
	1×10^{-2}	11.96	12.08	12.10	12.21	12.23	11.91	12.04	12.11	12.15	12.21
	2.5×10^{-2}	12.34	12.41	12.49	12.48	12.53	12.36	12.46	12.53	12.62	12.69
	5×10^{-2}	12.61	12.69	12.78	12.79	12.84	12.60	12.71	12.80	12.84	12.89
	1×10^{-1}	12.92	13.01	13.11	13.20	13.22	12.94	13.07	13.12	13.11	13.19
Gyrolite	5×10^{-3}	11.66	11.73	11.80	11.89	11.92	11.71	11.80	11.91	11.94	11.99
	1×10^{-2}	11.96	12.11	12.19	12.18	12.27	12.21	12.26	12.30	12.29	12.35
	2.5×10^{-2}	12.34	12.40	12.49	12.51	12.59	12.36	12.47	12.60	12.66	12.70
	5×10^{-2}	12.61	12.71	12.79	12.88	13.01	12.66	12.77	12.83	12.85	12.90
	1×10^{-1}	12.92	12.99	13.09	13.07	13.14	12.94	13.05	13.11	13.20	13.22

Table 3 Change in electrical conductivity ($\mu\text{moh.cm}^{-1}$) of alkali metals hydroxides on reaction with solids at different reaction times

Reaction time/h	Concn. of alkali metal (mol/l)	Xonotlite		Gyrolite	
		NaOH	KOH	NaOH	KOH
1	5×10^{-3}	12.02×10^4	15.04×10^4	11.92×10^4	15.66×10^4
	1×10^{-2}	14.13×10^4	13.51×10^4	15.52×10^4	15.38×10^4
	2.5×10^{-2}	16.72×10^4	20.04×10^4	19.2×10^4	20.32×10^4
	5×10^{-2}	17.70×10^4	18.36×10^4	18.4×10^4	19.40×10^4
	1×10^{-1}	19.22×10^4	19.95×10^4	18.54×10^4	17.64×10^4
6	5×10^{-3}	11.49×10^4	13.22×10^4	11.46×10^4	14.02×10^4
	1×10^{-2}	12.95×10^4	12.41×10^4	14.10×10^4	12.14×10^4
	2.5×10^{-2}	13.84×10^4	18.20×10^4	17.52×10^4	17.89×10^4
	5×10^{-2}	16.70×10^4	17.50×10^4	17.0×10^4	16.82×10^4
	1×10^{-1}	18.97×10^4	17.70×10^4	18.16×10^4	16.48×10^4
12	5×10^{-3}	10.95×10^4	9.68×10^4	10.76×10^4	12.24×10^4
	1×10^{-2}	12.10×10^4	12.10×10^4	12.90×10^4	10.69×10^4
	2.5×10^{-2}	12.4×10^4	17.0×10^4	15.84×10^4	17.0×10^4
	5×10^{-2}	16.26×10^4	16.24×10^4	15.67×10^4	16.32×10^4
	1×10^{-1}	17.12×10^4	17.52×10^4	17.07×10^4	15.95×10^4
24	5×10^{-3}	10.15×10^4	9.36×10^4	9.84×10^4	12.18×10^4
	1×10^{-2}	11.10×10^4	11.89×10^4	12.75×10^4	9.67×10^4
	2.5×10^{-2}	12.52×10^4	16.70×10^4	14.95×10^4	16.82×10^4
	5×10^{-2}	15.42×10^4	15.92×10^4	15.62×10^4	16.10×10^4
	1×10^{-1}	16.91×10^4	17.3×10^4	16.52×10^4	15.45×10^4

ner surface of the interlayer with higher concentrations of MOH, a $\text{M}^+ \rightleftharpoons \text{Ca}^{2+}$ exchange with in the interlayer would take place to a smaller extent¹⁶⁾. The rate of the exchange reaction generally increased with the increases of the reaction time up to 24 hrs in both xonotlite and/or gyrolite compounds. This is achieved from the kinetic uptake of Na^+ and K^+ **Fig. 5 (a and b)**, but at reaction time longer than 24 hrs, there is no significant change in the amounts of Na^+

or K^+ incorporated into these solids. This means that these cation exchange reactions reached the equilibrium state after 24 hrs.

Generally, the amounts of K^+ -ions uptaken by the solid (or exchanged with Ca^{2+}) have been found to be higher than as those in the case of Na^+ . Partial hydrolysis takes place at higher concentrations of MOH ($> 0.025 \text{ mol/l}$) via cleavage of Si-O-Si bonds (**Figs. 6 and 7**) facilitates

Table 4 Concentrations of alkali metals (M^+) hydroxides exchanged with Ca^{2+} from xonotlite and the calculated M^+/Ca^{2+} molar ratio

Reaction time/h	Initial concn. of MOH (mol/l)	NaOH			KOH		
		Concn. of Na^+ uptake (mmol/100 g)	Concn. of Ca^{2+} released (mmol/100 g)	Na^+/Ca^{2+} molar ratio	Concn. of K^+ uptake (mmol/100 g)	Concn. of Ca^{2+} released (mmol/100 g)	K^+/Ca^{2+} molar ratio
1	5×10^{-3}	3.2	3.16	1.02	3.6	3.7	0.97
	1×10^{-2}	10.0	9.5	1.04	10.3	10.8	0.95
	2.5×10^{-2}	14.7	15.0	0.97	14.9	15.2	0.98
	5×10^{-2}	23.3	23.8	0.98	23.4	24.4	0.95
	1×10^{-1}	28.8	29.5	0.97	28.9	30.1	0.96
6	5×10^{-3}	7.7	7.6	1.00	7.8	7.7	1.00
	1×10^{-2}	14.6	14.4	1.10	14.7	15.0	0.98
	2.5×10^{-2}	19.2	19.8	0.96	20.0	21.0	0.95
	5×10^{-2}	28.3	29.5	0.96	28.5	29.5	0.96
	1×10^{-1}	31.1	31.2	0.99	31.2	32.5	0.95
12	5×10^{-3}	12.6	12.4	1.01	13.4	13.2	1.01
	1×10^{-2}	18.3	17.6	1.04	18.7	19.3	0.96
	2.5×10^{-2}	22.3	22.8	0.97	22.9	24.1	0.95
	5×10^{-2}	32.8	33.1	0.99	33.6	34.8	0.96
	1×10^{-1}	34.4	35.7	0.96	35.3	36.2	0.97
24	5×10^{-3}	15.5	15.6	0.99	15.4	15.0	1.02
	1×10^{-2}	19.7	20.5	0.96	19.8	20.3	0.97
	2.5×10^{-2}	25.1	25.9	1.03	25.8	26.8	0.96
	5×10^{-2}	34.5	35.3	0.97	35.2	35.4	0.99
	1×10^{-1}	36.6	37.4	0.98	37.4	38.7	0.96

Table 5 Concentrations of alkali metals (M^+) hydroxides exchanged with Ca^{2+} from gyrolite and the calculated M^+/Ca^{2+} molar ratio

Reaction time/h	Initial concn. of MOH (mol/l)	NaOH			KOH		
		Concn. of Na^+ uptake (mmol/100 g)	Concn. of Ca^{2+} released (mmol/100 g)	Na^+/Ca^{2+} molar ratio	Concn. of K^+ uptake (mmol/100 g)	Concn. of Ca^{2+} released (mmol/100 g)	K^+/Ca^{2+} molar ratio
1	5×10^{-3}	4.2	4.1	1.02	4.9	5.30	0.96
	1×10^{-2}	11.3	11.2	1.01	11.5	11.2	1.02
	2.5×10^{-2}	15.6	15.5	1.01	16.3	16.4	0.99
	5×10^{-2}	25.9	27.0	0.9	26.26	27.0	0.97
	1×10^{-1}	28.9	29.3	0.98	29.8	27.7	1.07
6	5×10^{-3}	7.9	8.2	0.96	8.5	8.4	1.00
	1×10^{-2}	15.5	16.2	0.95	16.7	17.2	0.97
	2.5×10^{-2}	21.1	20.4	1.03	22.8	23.4	0.97
	5×10^{-2}	32.0	32.9	0.97	32.5	33.7	0.96
	1×10^{-1}	32.2	34.0	0.96	33.6	34.8	0.96
12	5×10^{-3}	13.1	12.6	1.04	13.4	12.7	1.05
	1×10^{-2}	18.9	18.8	1.00	19.6	21.1	0.97
	2.5×10^{-2}	23.4	23.0	1.02	23.6	21.1	0.97
	5×10^{-2}	34.8	35.3	0.98	35.5	36.9	0.96
	1×10^{-1}	36.5	37.1	0.98	37.7	38.3	0.98
24	5×10^{-3}	15.7	14.4	1.08	15.8	16.1	0.97
	1×10^{-2}	20.9	21.6	0.97	22.9	22.1	1.03
	2.5×10^{-2}	27.0	27.1	0.99	28.2	29.0	0.97
	5×10^{-2}	36.6	37.8	0.96	37.8	39.7	0.95
	1×10^{-1}	39.9	41.5	0.96	40.9	42.0	0.97

(a)

Fig. 6(a) A double dreierkette from xonotlite structure²⁵⁾.

(b)

Fig. 6(b) Structure of xonotlite projection along b-axis (the chain direction)²⁵⁾.
 (○ = Ca²⁺, ○ = Si⁴⁺, ● = OH-group)

the cation exchange process $\text{Ca}^{2+} \rightleftharpoons \text{M}^{+}$ ¹⁶⁾. A cleavage of Si–O–Si bonds would consume minor amounts of MOH according to:

The negative charges on the silicate chains will be balanced by M⁺ at the cleaved positions. In the reaction of 11.3 Å-tobermorite with MOH, it was reported that the cleaving of Si–O–Si bonds may lead to additional small pores or channels of different diameters in the solids structure¹⁶⁾. This may facilitate the exchange of interlayer Ca²⁺ ions. Such cavities accommodate additional M⁺ ions in the solid structure.

XRD results due to the reaction of Na⁺ and/or K⁺ with xonotlite and gyrolite compounds (**Figs. 1 and 2**) showed that these solids generally did not lose their crystallinity and their basal spacing did not change in the $\text{Ca}^{2+} \rightleftharpoons \text{M}^{+}$ exchange process.

The data of EDAX resulting from the reaction of Na⁺ and K⁺-ions with xonotlite and reaction of K⁺-ions with gyrolite solids at 0.1 M MOH concentration are given in **Figs. 3b and 4b**. These data demonstrate the existences of K_α radiations of Ca²⁺ and Si(+IV) in addition to Na⁺ and/or K⁺. This confirms the incorporation of alkali metal ions in calcium silicates hydrate structure and exchanges with their Ca²⁺-ions.

In conclusion, xonotlite and gyrolite as crystalline mem-

Fig. 7 Schematic drawing of the crystal structure of gyrolite as viewed along a-axis by Merlino²⁶⁾. S₁ and S₂ are different kinds of silicate anions sheet, and (O) is calcium layer, (x) is calcium, and water mixed layer in the structure.

bers of calcium silicate hydrate compounds prepared under hydrothermal conditions can be used as cation exchangers for the separation of alkali metal hydroxides MOH (Na⁺ and K⁺) from their aqueous solutions (or pollutant) via $\text{Ca}^{2+} \rightleftharpoons \text{M}^{+}$ exchange process. They have cation exchange capacities amounting to 41.70 and 44.40 meq/100 g respectively. The amount (mmol/100 g) of alkali metals uptaken by these solids increases with the increase of MOH concentration and/or time of reaction. This uptake reached equilibrium state after 24 hrs.

Gyrolite solid can uptake a maximum amount (mmol/100 g) of 40.96 of K⁺ and 39.97 of Na⁺, while 37.44 and 36.74 (mmol/100 g) in xonotlite respectively after 24hrs reaction time. Generally the amounts of K⁺-ions entered into the lattice structure of the solid were higher than Na⁺, due to the effect of relative activity of the cation and the decrease of K⁺ hydration radius. The $\text{Ca}^{2+} \rightleftharpoons \text{M}^{+}$ exchange reaction was found to be stoichiometrically one in dilute concentrations of MOH up to 0.025 mol/l, and shifted slightly less than this stoichiometric value when higher MOH concentrations were used. This is due to the presence of limited partial hydrolysis for Si–O–Si bonds in SiO₄ tetrahedral lattice structure of the solids and hence extra Ca²⁺-ions released.

The observed affinities of xonotlite and gyrolite compounds for Na⁺ and/or K⁺-ions could be utilized in the separation of the cations from aqueous solutions.

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