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# SYNTHESIS OF NOVEL Na-RICH MICA AND SELECTIVE STRONTIUM ION EXCHANGE AND FIXATION

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## ABSTRACT

A novel swelling mica of composition, $Na_{2.94}(Mg_{5.55}Ti_{0.07}Fe_{0.04})(Al_{2.07}Si_{5.83})O_{20}F_4{\cdot}1.72H_2O$, was synthesized from kaolinite, and this mica was found to be very selective for Sr with a high capacity for uptake. Apparently, both tetrahedral and octahedral sheets contribute to the total negative charge in this mica. A relatively low-temperature heat treatment at 250°C of the Sr-exchanged mica resulted in the collapse of the hydrated interlayer spacings of the mica to immobilize strontium in a stable unhydrated phase.

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## INTRODUCTION

There is a continuing need for developing new ion-exchange materials for the remediation of aqueous radioactive wastes arising from nuclear power stations, military sites, reprocessing plants, and research centers. Naturally occurring cation exchangers such as clays and zeolites have been used to decontaminate and dispose the radioactive species (1,2). There has been a great deal of effort to develop high-performance synthetic cation exchangers for the uptake of $^{90}$Sr and $^{137}$Cs and their immobilization (3–10), because these elements constitute both the major heat producers and biohazards in nuclear wastes for the first 600 years or so (11). Removal of these elements would virtually eliminate concern for any thermally induced problems with the waste form and geologic repository chosen for the residual fission product fraction. It is also needed for remediation process of ground water at the Hanford site to prevent contamination of the Columbia River (12).

The synthetic clay mineral, "Na-4-mica", is a sodium fluorophlogopite mica of a theoretical chemical composition $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot x\,H_2O$ with high layer charge density (13–24). Na-4-mica contains an unusually large number of four interlayer cations per unit cell. This mica is unique because no other mica with more than two interlayer cations per unit cell had ever been observed before. Micas are distinguished from smectites or vermiculites by their higher layer charge density (25). The interlayer cations in naturally occurring micas are trapped due to electrostatic bonding resulting from high-layer charge density and do not normally swell in water. Therefore, ion exchange reactions with the interlayer cations do not readily occur. Synthetic micas, which swell in water, with ion exchange capacities of 200–250 meq $(100\,g)^{-1}$ have been prepared recently and these are of considerable interest (26–29). Na-4-mica, however, has a higher Al(III) content but exhibits unusual swelling behavior and selective cation-exchange properties potentially useful in hazardous cation separations from solutions (13–24). The Na-4-mica has a theoretical cation-exchange capacity of 468 meq $(100\,g)^{-1}$ on anhydrous basis but readily becomes hydrated on contact with water or even in moist air at ambient conditions.

Paulus et al. (15) first reported the sol–gel synthesis of a very fine and pure phase of Na-4-mica, which is essential for practical applications. They further showed that the mica so-produced had high cation-exchange selectivities for many divalent transition-metal ions and for strontium and barium (16). This synthetic method, however, is not cost-effective because of the use of expensive chemicals such as tetraethoxysilane and the long and tedious procedure. Recently, we found a new route for the synthesis of Na-4-mica from naturally occurring kaolinite (18–24). Phase pure and fine Na-4-mica is easily and economically prepared from a precursor mixture of NaF, ultrafine MgO (or magnesium nitrate), and kaolinite, the latter serving as a cost-effective aluminosilicate source with the desired 1:1 Si to Al molar ratio. We also reported the synthesis of another new swelling mica phase, $Na_2Mg_6Al_2Si_6O_{20}F_4{\cdot}x\,H_2O$ (hereafter referred to as "Na-2-mica") by the solution–sol–gel process and reported that this phase is also an excellent Sr ion exchanger (30).

A very fine Na-4-mica phase ($<1\,\mu$m) is a highly selective Sr ion exchanger with a large exchange capacity (CEC) for Sr ion at room temperature (15). However, the Sr uptake kinetics are very slow and the exchange reactions were carried out for 4 weeks to achieve a steady state (15,18,22). In the present work, we attempted the synthesis of Na-2-mica phase by modification of the simple and economical synthetic process of Na-4-mica from kaolinite but discovered the formation of a new swelling Na-rich mica with about three interlayer $Na^+$ ions per unit cell. This mica of new composition (hereafter referred to as "Na-3-mica") shows much faster Sr uptake kinetics and a larger Sr ion exchange capacity than the Na-4-mica at room temperature.

## EXPERIMENTAL

### Preparation of Micas

The novel Na-rich mica was prepared in the same general way as the Na-4-mica, which was previously prepared from a precursor mixture of naturally occurring kaolinite, magnesium nitrate (or ultrafine MgO), and NaF at 800–890°C (18–24). Here, we attempted to synthesize $Na_2Mg_6Al_2Si_6O_{20}F_4{\cdot}x\,H_2O$ (Na-2-mica) by the modification of this synthetic process. In the modified procedure, $SiO_2$ was added to kaolinite, which has a theoretical chemical composition of $Al_2Si_2O_5(OH)_4{\cdot}n\,H_2O$, in order to obtain the stoichiometric composition of Al–Si = 1:3. A poorly crystallized kaolinite of composition 47.9% $SiO_2$, 38.3% $Al_2O_3$, 2.08% $TiO_2$, 0.98% $Fe_2O_3$, 0.15% FeO, and 0.03% MgO (supplied by Georgia Kaolin Company through W. D. Johns, Dept. of Geology, Univ. of Missouri, Columbia, MO 65201), was used for the synthesis of the new mica. Appropriate amounts of the kaolinite, $Mg(NO_3)_2{\cdot}6H_2O$ and $SiO_2$ were mixed to obtain a stoichiometric composition (Mg–Si–Al molar ratio = 3:1:3). The water content of the kaolinite was previously determined to be 14.16 wt% by thermal analysis using TG DTA 2010, Mac Science. Then, it was mixed with NaF with a molar ratio of NaF/kaolinite[$Al_2Si_2O_5(OH)_4$] of 8. NaF not only acts as a flux for the high-temperature crystallization of mica but it is also a source of sodium and fluorine. The mixture was thoroughly homogenized using a pestle and mortar, and transferred to an alumina vessel. The precursor mixture was calcined for 24 hr at 850°C in air using a programmed furnace. The resulting solids were ground and washed in deionized water several times to remove excess NaF. Any remaining impurity phases such as insoluble fluoride salts were then removed with repeated washings using saturated boric acid solution (15). Then, the solid was washed with 1 *M* NaCl solution three times to completely saturate all the exchange sites with $Na^+$. The mica thus prepared was finally washed with deionized water, dried at 60°C in an oven for 2–3 days, and stored in a desiccator over silica gel at room temperature.

Na-4-mica (ideal composition of $Na_4Mg_6Al_4Si_4O_{20}F_4 \cdot x\,H_2O$) was also prepared by a similar (original) procedure (23,24) from kaolinite at 850°C for comparison. Appropriate amounts of the kaolinite and $Mg(NO_3)_2 \cdot 6H_2O$ were mixed to obtain a stoichiometric composition (Mg–Si–Al molar ratio = 3:2:2). Then it was mixed with NaF with a molar ratio of NaF/kaolinite[$Al_2Si_2O_5(OH)_4$] of 4. The mixture was thoroughly homogenized using a pestle and mortar, and transferred to an alumina vessel. The precursor mixture was calcined for 24 hr at 850°C in air using a programmed furnace. The resultant solid thus prepared was ground, washed, and $Na^+$-saturated by the same procedures used for the above Na-3-mica. The Na-4-mica thus prepared was finally washed with deionized water, dried at 60°C in an oven for 2–3 days, and stored in a desiccator over silica gel at room temperature.

The Sr-saturated Na-3-mica was obtained by treatment of the Na-3-mica with a 1 *M* $SrCl_2$ solution at 70°C for 8 days. The solution was renewed daily. The product was washed with deionized water and dried at 60°C in an oven for 2–3 days. It was finally stored in a desiccator over silica gel at room temperature.

## Characterization of Products

Powder x-ray diffraction (XRD) was carried out to check for phase purity and to determine the basal spacings of mica using a Rigaku RAD-γA diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) was used to determine the crystallite size and shape (EPMA-8705, Simadzu Corporation, Kyoto, Japan). The particle size distribution was determined in a 0.3 wt% sodium hexametaphosphate solution using a laser diffraction (SALD-3000, Laser Diffraction Particle Size Analyzer, Shimadzu) technique. For the Na-3-mica, all the metal oxide contents, sodium, aluminum, silicon, magnesium, iron, and titanium oxide contents, were determined by lithium borate fusion and chemical analyses using atomic emission spectrometry (SpectraSpan III instrument). For the Sr-saturated Na-3-mica, sodium and strontium oxide contents were determined by the same method. Water contents of the micas were determined by thermal analysis. In the TG-curves, the rapid weight loss occurred up to around 110°C and then the weight gradually decreased up to 250–280°C. Both weight losses were due to water release.

## Comparison of the Distribution Coefficient ($K_d$) for Alkaline Earth Metal Ions

The distribution coefficient, $K_d$, was determined as follows. A measured amount (20 mg) of the Na-3-mica (anhydrous basis) was equilibrated with 25 $cm^3$ of a 0.5 N NaCl containing 0.0001 N $MCl_2$ ($M^{2+} = Sr^{2+}$, $Ba^{2+}$, $Mg^{2+}$, or $Ca^{2+}$) at room temperature: each solution for $K_d$ measurement contained only one kind of alkaline earth metal. After 24 hr, the solid and solution phases were separated by centrifugation. The solutions were analyzed for $M^{2+}$ to determine the amount remaining in solution by atomic emission spectroscopy (ICP, Seiko Instruments SPS-1500 V). The uptake of $M^{2+}$ was determined from the difference in the concentration between the sample and the reference. The $K_d$ was calculated by the following equation:

$$K_d = \frac{[\text{amount of metal ions in exchanger (meq/g)}]}{[\text{amount of metal ions in solution (meq/cm}^3)]} \quad (1)$$

The experiments were conducted in triplicate to check for reproducibility. The errors in the triplicates were about ± 5%.

## Sr Uptake Kinetics with Mica

The Sr uptake kinetics were determined in batch experiments using mica. Mica sample of about 25 mg (anhydrous basis) was added into 25 $cm^3$ of 0.005 *M* $SrCl_2$ in polypropylene centrifuge tubes. The centrifuge tubes were agitated continuously on a reciprocating shaker at room temperature for different periods. Then, the solid and solution phases were separated by centrifugation. The solutions were analyzed for $Sr^{2+}$ remaining in solution by atomic emission spectrometry. Three replicates were used for each duration to check for reproducibility. The errors in the triplicates were about ± 5%.

## Sr Leaching Test from Sr-Saturated Na-3-Mica

With the Sr-saturated Na-3-mica, Sr leaching test was carried out using batch experiments. Sr-saturated mica of about 25 mg (anhydrous basis) was added to 25 $cm^3$ of 0.5 *M* NaCl in centrifuge tubes. The centrifuge tubes were agitated continuously on a reciprocating shaker at room temperature for different periods. Then, the solid and solution phases were separated by centrifugation. The solutions were analyzed for $Sr^{2+}$ remaining in the solution by atomic emission spectrometry. Three replicates were used for each duration to check for reproducibility. The errors in the triplicates were about ±5%.

The Sr-saturated Na-3-mica was heated at 250°C for a day in air. The heat-treated Sr-saturated Na-3-mica also underwent the Sr leaching test in the same way and the results were compared with those for nonheat-treated Sr-saturated Na-3-mica.

## RESULTS AND DISCUSSION

### Characterization of Na-3-Mica

The XRD pattern of the resultant solid prepared by the modified procedure, using the precursor mixture of kaolinite, magnesium nitrate, $SiO_2$, and NaF (Mg–Si–Al molar ratio = 3:1:3), is shown in Fig. 1. A strong peak was observed at $d = 12.11$ Å, which can be assigned to the (001) reflection of a hydrated mica with a single sheet of interlayer water (13). Small peaks observed at $d = 6.09$, 4.05, and 3.04 Å are assigned to (002), (003), and (004) reflections of $c$-axis spacing of the hydrated mica. This $c$-axis spacing ($d = 12.11$Å) was almost the same value as that of the hydrated Na-4-mica (15–24). In the hydrated Na-4-mica, the interlayer $Na^+$ ions are accommodated in the ditrigonal holes above and below the central single sheet of interlayer water (13). This hydrated interlayer structure leads to the narrow interlayer spacing of about 2 Å in comparison to other 2:1 phyllosilicates with low layer charge densities, such as smectite, which have the hydrated interlayer spacings of 4–5 Å. This mica

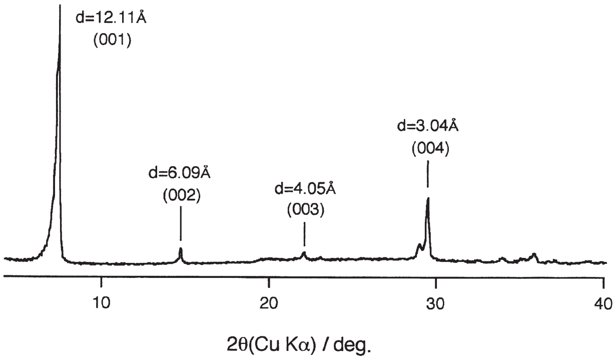

***Figure 1.*** XRD pattern of the mica prepared by the modified procedure, using the precursor mixture of kaolinite, magnesium nitrate, $SiO_2$, and NaF (Mg–Si–Al molar ratio = 3:1:3).

prepared by the modified procedure is considered to have the similar hydrated interlayer structure to Na-4-mica.

The metal oxide and water contents of the mica prepared by the modified procedure are given in Table 1. The Na/Al molar ratio of the mica was 1.4, which is much higher than that expected for Na-2-mica (Na/Al molar ratio $= 1$). The structural formula was estimated from the metal oxide and water contents, based on $O_{20}F_4$ expected for 2:1 layer alminosilicate, to be $Na_{2.94}(Mg_{5.55}Ti_{0.07}Fe_{0.04})_{oct}(Al_{2.07}Si_{5.83})_{tet}O_{20}F_4 \cdot 1.72H_2O$. Iron and titanium ions were estimated to locate in the octahedral sheets (31). In this formula, the cation number occupying the tetrahedral sites was very close to the tetrahedral site number of 8 for $O_{20}F_4$. However, only 5.66 of the cations occupied the octahedral sites per unit cell although the octahedral site number is 6, indicating that some octahedral sites are vacant. The octahedral vacancies can also create the negative layer charge as well as the substitution of tetrahedral $Si^{4+}$ ions by $Al^{3+}$ ions. Both the negative layer charges in the tetrahedral and octahedral sheets are considered to enable the incorporation of about three interlayer $Na^+$ ions in this mica.

This Na-3-mica prepared by the modified procedure was cation-exchanged with $Sr^{2+}$ ions at 70°C. In the XRD pattern of the Sr-saturated Na-3-mica thus prepared, only the peaks due to the hydrated mica appeared (Fig. 2a). The basal spacing slightly increased to $d = 12.19$ Å. The strontium and sodium oxide contents of the Sr-saturated mica are also given in Table 1. In comparison to these metal oxide contents of the original Na-3-mica, the sodium oxide content decreased with an increase in the strontium oxide content (Table 1), indicating the $2Na^+ \rightarrow Sr^{2+}$ exchange in the mica. The Sr/Na molar ratio of the Sr-saturated mica was 3.5. This indicates that 88% of the interlayer $Na^+$ ions (2.94 per unit cell of the original mica) were exchanged by $Sr^{2+}$ ions. Assuming that the tetrahedral and octahedral composition of the mica has not changed by this ion exchange treatment and is the same as that of the original mica, the chemical formula of the Sr-saturated mica can be estimated to be $Sr_{1.29}Na_{0.37}(Mg_{5.55}Ti_{0.07}Fe_{0.04})_{oct}(Al_{2.07}Si_{5.83})_{tet}O_{20}F_4 \cdot 3.15H_2O$. The strontium oxide content from this chemical formula was 11.1%, which was almost consistent with the observed value (Table 1). The CEC for Sr ion at 70°C attained about 313 meq $(100\,g)^{-1}$ of the Na-3-mica on anhydrous basis. The maximum CEC value of Na-2-mica is estimated to be only 247 meq $(100\,g)^{-1}$ on anhydrous basis from the ideal chemical composition. Therefore, this new mica prepared by the modified procedure obviously had a higher layer charge than the Na-2-mica. Based on the estimated chemical formula of Na-3-mica, the theoretical CEC was estimated to be 357 meq $(100\,g)^{-1}$ on anhydrous basis.

The SEM micrograph of the mica shows plate-like and pseudo hexagonal crystallites (Fig. 3a). The crystallite size is around $0.2-2\,\mu m$ and many crystallites agglomerated to form massive grains of particles. The particle size distribution was determined by laser diffraction and is shown in Fig. 4a. The size distribution ranged from 0.3 to 15 $\mu m$ and the average particle size is 1.8 $\mu m$.

***Table 1.*** Metal Oxide and Water Contents of the Na-3-Mica and Sr-Saturated Na-3-Mica

| | Content[a] (wt%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Materials | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | MgO | $Na_2O$ | SrO | $H_2O$ |
| Na-3-mica (Na-saturated) | 41.5 | 12.5 | 0.68 | 0.38 | 26.5 | 10.8 | — | 3.6 |
| Sr-saturated Na-3-mica | — | — | — | — | — | 1.0 | 11.7 | 7.4 |

[a] Water contents were determined by thermal analysis. All the metal oxide contents were determined by lithium borate fusion and chemical analyses using atomic emission spectrometry.

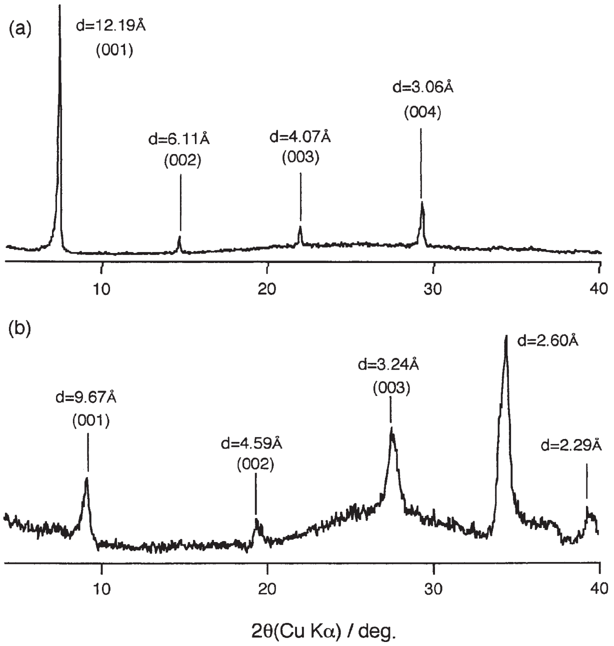

***Figure 2.*** XRD patterns of the Sr-saturated Na-3-micas (a) before and (b) after the heat treatment at 250°C.

## Cation-Exchange Properties of Na-3-Mica

The distribution coefficients ($K_d$) for the exchange of $Sr^{2+}$, $Ba^{2+}$, $Ca^{2+}$, and $Mg^{2+}$ from a background solution of 0.5 N NaCl are presented in Table 2: the initial concentration of the alkaline earth metal in the solution was 0.0001 N. This mica has much higher selectivities for $Ba^{2+}$ and $Sr^{2+}$ than for the other alkaline earth metals.

Curve A in Fig. 5 shows the Sr uptake kinetics with this Na-3-mica in a 0.005 $M$ $SrCl_2$ solution. The forward $Sr^{2+}/2Na^{+}$ exchange was equilibrated after one week and about 64% of the interlayer $Na^{+}$ ions was exchanged by $Sr^{2+}$ at room temperature. The Sr-ion exchange capacity reached 227 meq $(100\,g)^{-1}$.

These Sr uptake kinetics with the novel Na-3-mica was compared to that with the Na-4-mica prepared by a similar (original) procedure using the precursor mixture of kaolinite, magnesium nitrate, and NaF without $SiO_2$ (Mg–Si–Al molar ratio = 3:1:3). The chemical composition of the Na-4-mica phase was previously determined by the x-ray fluorescence analysis to be $Na_{4.17}Mg_{6.07}Al_{3.94}Si_{3.97}O_{20}F_4$ (32). The SEM micrograph and the particle size

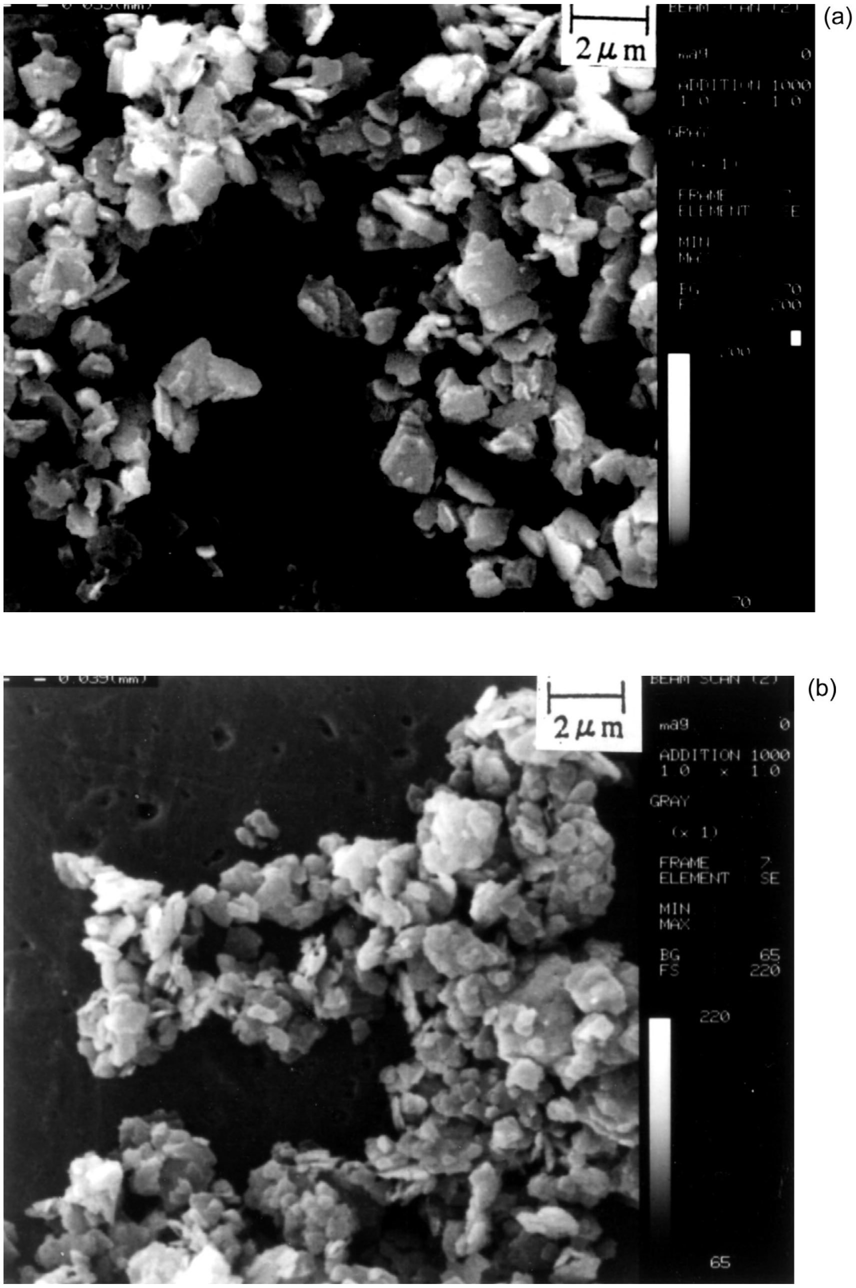

*Figure 3.* SEM micrographs of (a) the novel Na-3-mica and (b) the Na-4-mica.

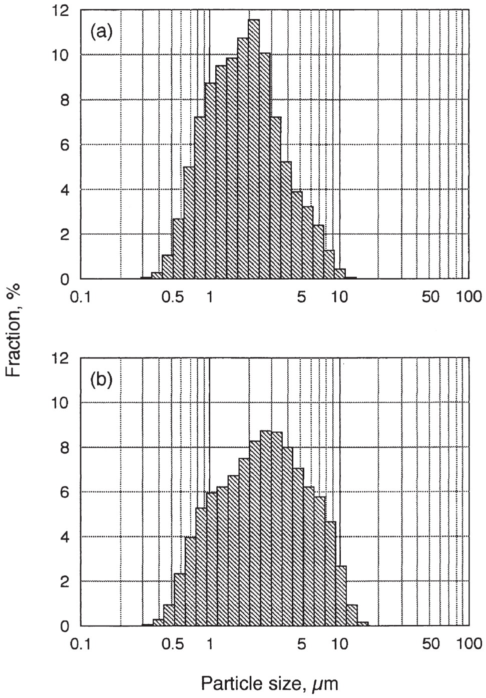

***Figure 4.*** Particle size distribution of (a) the novel Na-3-mica and (b) the Na-4-mica estimated from laser diffraction.

distribution for the Na-4-mica are shown in Figs. 3b and 4b, respectively. Na-4-mica has the same crystallite size (Fig. 3b) as that of the novel Na-3-mica (Fig. 3a). The average particle size (2.5 μm) of the Na-4-mica (Fig. 4b) is almost similar to that of the novel Na-3-mica (Fig. 4a). With this Na-4-mica, it took more than 4 weeks to achieve steady-state of Sr uptake under the same reaction conditions (Curve B in Fig. 5). Sr ion exchange capacity of the Na-4-mica, which was attained after 4 weeks, is 202 meq $(100\,g)^{-1}$, which is smaller than the CEC of the novel Na-3-mica [227 meq $(100\,g)^{-1}$] whose capacity was attained only in 3 days. The layer charge density in the novel Na-3-mica (about −3 per unit cell) is lower than that in Na-4-mica (−4 per unit cell), which apparently facilitates the diffusion of $Sr^{2+}$ ions in the interlayer spacings of the Na-3-mica.

The leaching test of Sr ion from the Sr-saturated Na-3-mica was carried out in a 0.5 *M* NaCl solution at room temperature (Curve A in Fig. 6). About 30% of the Sr ions were released from the mica. We heat-treated the Sr-saturated Na-3-mica at 250°C in order to collapse the hydrated interlayer spacings of the

***Table 2.*** Distribution Coefficients ($K_d$) of the Na-3-Mica for Alkaline Earth Metals of $Ba^{2+}$, $Sr^{2+}$, $Mg^{2+}$, and $Ca^{2+}$

| Exchanging Cation | $K_d$ ($cm^3 g^{-1}$) |
|---|---|
| $Ba^{2+}$ | $2.45 \times 10^6$ |
| $Sr^{2+}$ | $1.99 \times 10^5$ |
| $Mg^{2+}$ | $2.08 \times 10^4$ |
| $Ca^{2+}$ | $7.30 \times 10^4$ |

The equilibrium pH were 9.3, 9.5, 9.5, and 9.4 for $Ba^{2+}$, $Sr^{2+}$, $Mg^{2+}$, and $Ca^{2+}$, respectively.

mica by dehydration. It was expected here that collapse of the hydrated interlayer region achieves effective strontium fixation, as the strontium becomes trapped into a more conventional trioctahedral mica structure similar to the barium interlayered mica, kinoshitalite, $Ba_2(Mg, Mg, Al)_6Si_4Al_4O_{20}(OH, F)_4$, which is an extremely stable phase because the high coulombic forces that span the interlayer region effectively hold it very tightly closed (33). Figure 2b shows the XRD pattern of the Sr-saturated Na-3-mica after the heat treatment. The basal spacing decreased from $d = 12.19$ to 9.67 Å, indicating the formation of the unhydrated mica phase. The Sr leaching test for this unhydrated Sr-saturated mica showed that only 8% of the interlayer Sr ions was released and the rest was trapped in the interlayer of the unhydrated mica phase (Curve B in Fig. 6). The

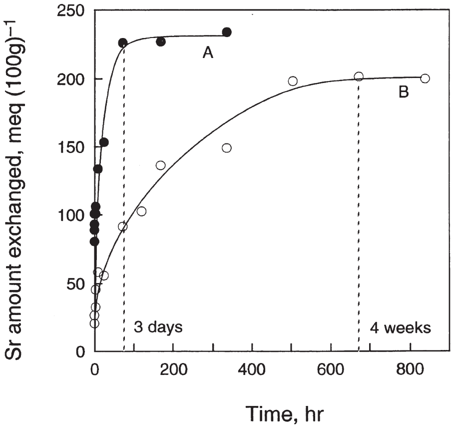

***Figure 5.*** Sr uptake kinetics by the novel Na-3-mica (Curve A) and the Na-4-mica (Curve B) from 0.005 *M* $SrCl_2$ solution.

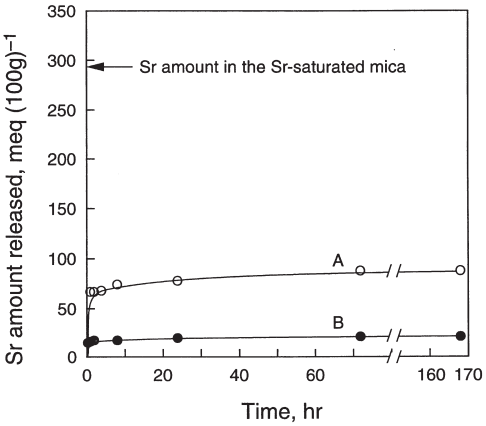

***Figure 6.*** Time variations of an amount of Sr ions released from the Sr-saturated Na-3-micas non-heat-treated (Curve A) and heat-treated (Curve B).

small amount of $Sr^{2+}$ ions released was probably due to those located on the external surface and edges of the mineral.

## CONCLUSION

A novel swelling mica, which had about three interlayer $Na^+$ ions per unit cell, was synthesized by the crystallization of a precursor mixture of kaolinite, magnesium nitrate, $SiO_2$, and NaF flux at 850°C. The crystallite size was around 0.2–2 $\mu$m and the average particle size was 1.8 $\mu$m. This new cation exchanger showed much higher selectivities for Sr and Ba than for Mg and Ca. In this novel Na-3-mica whose layer charge density ($-3$ per unit cell) is lower than that of Na-4-mica ($-4$ per unit cell), the diffusion of $Sr^{2+}$ ion in the interlayer spacings is highly facilitated to improve the Sr uptake kinetics compared to that in the Na-4-mica. A higher CEC of 227 meq (100 g)$^{-1}$ was attained for Sr ion in 3 days with this new mica while the Na-4-mica attained a CEC of 202 meq (100 g)$^{-1}$ for Sr ion after 4 weeks. The unhydrated Sr-exchanged phase, which was prepared by the low-temperature dehydration, showed extremely low Sr leachability. This selective Sr-ion exchanger is expected to be useful for $^{90}Sr$ removal and its immobilization.

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