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Novel Na-3-Mica: Alkaline Earth Cation Exchange and Immobilization

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ABSTRACT

The cation-exchange capacities for the alkaline earth metals Ba, Mg, and Ca, and their immobilization in the interlayers of a novel swelling fluorine mica (Na-3-mica) with a high-layer-charge density were studied. The mica was fully exchanged or saturated with Ba, Mg, and Ca ions and the cation-exchange capacities were determined to be 246, 338, and 322 meq $(100\,g)^{-1}$, respectively, on anhydrous basis of mica. The chemical analyses of the saturated micas indicated that about three exchangeable interlayer sodium ions per unit cell existed in the mica as

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a result of the total negative layer charge due to both Mg vacancies in octahedral sheets and Al substitution in tetrahedral Si sheets of the silicate. The Ba, Mg, and Ca leachabilities of the saturated micas were investigated in 0.5 M NaCl background solutions at room temperature and these were compared to the Sr leachability of the Sr-saturated mica. The degree of the cation immobilization in the interlayers increased in the order of $Ca < Sr < Ba < Mg$. This could be explained by the interlayer spacings and structures of the saturated micas.

INTRODUCTION

There are many methods for the immobilization and disposal of nuclear aqueous wastes produced during the nuclear fuel cycle.[1] Preconcentration and/or separation of toxic radionuclides from aqueous wastes are usually performed through adsorption or ion exchange.[1,2] For this reason, high-performance synthetic inorganic cation exchangers have been developed especially for the uptake of ^{90}Sr and ^{137}Cs and their fixation.[3–5]

Mica is a 2:1 phyllosilicate clay mineral, each layer consisting of an octahedral sheet sandwiched between two tetrahedral sheets, and is distinguished from smectites or vermiculites by its higher layer charge density. Due to the high layer-charge density, naturally occurring micas do not swell in water, and as a result, ion-exchange reactions with the interlayer cations do not easily occur. Synthetic micas, which swell in water, with cation-exchange capacities of about $200-250\,\text{meq}\,(100\,\text{g})^{-1}$ have been prepared and these are of considerable interest.[6–8] In recent years, the synthetic clay mineral "Na-4-mica" (ideal chemical composition $Na_4Mg_6Al_4Si_4O_{20}F_4\cdot xH_2O$) has been extensively investigated, which has a large theoretical cation-exchange capacity of $468\,\text{meq}\,(100\,\text{g})^{-1}$ on anhydrous basis and readily becomes hydrated on contact with water or even in moist air at ambient conditions[9–20] because of its special structure.[9]

A very fine Na-4-mica phase was successfully synthesized by a solution-sol-gel process[10,11] and also by a new economical synthetic route from naturally occurring kaolinite.[18] This Na-4-mica is a highly selective Sr cation exchanger with a large Sr-uptake capacity [about $200\,\text{meq}\,(100\,\text{g})^{-1}$ when 0.005 M $SrCl_2$ was used] at room temperature.[10,19] The Sr uptake kinetics are, however, very slow and the exchange required about four weeks to achieve a steady state. Recently, we have attempted the synthesis of $Na_2Mg_6Al_2Si_6O_{20}F_4\cdot xH_2O$ (Na-2-mica) by the modification of the economical synthetic method using kaolinite for Na-4-mica and found that the synthesized swelling-mica showed much larger and faster Sr ion uptake than the Na-4-mica.[20] However, the chemical analyses of the synthesized mica and its cation-exchange capabilities for Sr showed that this new mica had a larger number of exchangeable interlayer sodium ions per unit cell than those expected from a theoretical Na-2-mica. This high CEC [313 meq $(100\,g)^{-1}$ on anhydrous basis] indicated that about three sodium ions are located in the interlayers per unit cell (hereafter referred to as Na-3-mica). We suggested that in this Na-3-mica, the Mg vacancies in octahedral sheets contributed to the total negative layer charge in addition to that created by Al substitution in tetrahedral Si sheets. It was also found that a relatively low-temperature heat treatment at 250°C of the Sr-exchanged mica resulted in collapse of the hydrated interlayers of the mica to immobilize strontium in a stable anhydrous phase. This mica can be expected to be useful for ^{90}Sr removal and its immobilization.

In this paper, the cation-exchange capacities of this novel Na-3-mica for the alkaline earth metals Ba, Mg, and Ca are presented and these results support that this mica has about three interlayer exchangeable sodium ions per unit cell. The Ba, Mg, and Ca leachabilities from this Na-3-mica were also investigated in comparison to the Sr leachability previously reported.[20] The leachabilities are shown to be related to many factors, such as the hydrated ionic radius of the desorbing cations in liquid and in the interlayer spacings and structures of the exchanged mica.

EXPERIMENTAL

Preparation of Na-3-Mica

The Na-3-mica was prepared from a precursor mixture of naturally occurring kaolinite, magnesium nitrate, SiO_2, and NaF at 850°C, as previously reported.[20] Our attempt to synthesize Na-2-mica of the chemical composition $Na_2Mg_6Al_2Si_6O_{20}F_4{\cdot}xH_2O$ yielded the Na-3-mica instead. The following procedure was used[20]: A poorly crystallized kaolinite [the ideal chemical composition of $Al_2Si_2O_5(OH)_4$] 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, Department of Geology, University of Missouri, Columbia, MO), was used for the synthsis of the mica. In order to obtain the stoichiometric composition of Al:Si:Mg = 1:3:3, SiO_2 and $Mg(NO_3)_2{\cdot}xH_2O$ were added to kaolinite. The water content of the kaolinite was previously determined to be 14.16 wt.% by thermal analysis using TG DTA 2010, Mac Science. Then, the mixture was mixed with NaF with a molar ratio of NaF/kaolinite[$Al_2Si_2O_5(OH)_4$] of 8. Sodium flouride 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 thus prepared was thoroughly homogenized using a pestle and mortar and transferred to an alumina vessel. The precursor mixture was reacted for 24 hr at 850°C in air using a programmed furnace. The resulting solid was 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. Then, the solid was washed with 1 M NaCl solution three times to completely saturate all the exchange site with Na^+ ions. The mica thus prepared was finally washed with deionized water. Immediately after the solid and solution phases were separated by centrifugation, powder x-ray diffraction (XRD) was carried out to check for phase purity and to determine the basal spacings of the swelling mica using a Rigaku RAD-γA diffractometor with CuK_α radiation because the swelling mica phase may lose the interlayer water to some extent on exposure to dry air for a long period. The mica was finally dried at 60°C in an oven for 2–3 days, and stored in a desiccator over silica gel at room temperature for use in chemical analysis and cation exchange experiments.

Preparation of Ba, Mg, and Ca Fully Exchanged (Saturated) Na-3-micas

The Na-3-micas were fully exchanged with Ba, Mg, or Ca ions in the same way that was used for the preparation of the Sr-saturated mica in our previous paper[20] as follows: The Na-3-mica was soaked in a 1 M MCl_2 (M = Ba, Mg, or Ca) solution at 70°C for 8 days. The solution was renewed daily. The M-saturated mica was washed with deionized water. Immediately after centrifuging, powder x-ray diffraction was carried out to determine the basal spacings of the exchanged mica. It was finally dried at 60°C in an oven for 2 to 3 days and stored in a desiccator over silica gel at room temperature for use in chemical analysis and ion-exchange experiments.

Characterization of Micas

Scanning electron microscopy (SEM) of the Na-3-mica was used to determine the crystallite size.[20] The crystallite size was around 0.2–2 μm and many crystallites agglomerated to form massive grains of particles [See Fig. 3a in Ref.[20]]. The particle size distribution determined by laser diffraction was also shown in the previous paper [See Fig. 4 in Ref.[20]]. The average particle size was 1.8 μm. The metal oxide contents of micas were determined by lithium-borate fusion and chemical analyses using atomic-emission spectrometry (SpectraSpan III instrument). Water contents of the micas were determined by thermal analysis.

Ba-, Mg-, and Ca-Leaching Tests for the Exchanged Micas

Ba-, Mg-, and Ca-leaching tests were carried out using batch experiments in the same way as previously used for the Sr-leaching test for the Sr-saturated mica.[20] Twenty five milligram of the M-saturated mica 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 Ba, Ca, or Mg ions remaining in solution by atomic-emission spectrometry. Three replicates were used for each duration to check for reproducibility. The errors in the triplicates were within ± 5%. Immediately after centrifuging, the solid phase was subjected to powder x-ray diffraction.

RESULTS AND DISCUSSION

The metal-oxide contents of the M-saturated micas, determined by the lithium–borate fusion method, are given in Table 1. The structural formulas were estimated from the metal-oxide and water contents based on $O_{20}F_4$ expected for 2:1 layer aluminosilicate (Table 2). In the previous paper,[20] the chemical composition of the original Na-3-mica was determined to be $Na_{2.94}(Mg_{5.55}Ti_{0.07}Fe_{0.04})_{oct}(Al_{2.07}Si_{5.83})_{tet}O_{20}F_{4}$. In this formula of the original mica, 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+} by Al^{3+}. Both the negative layer charges in the tetrahedral and octahedral sheets are responsible for the incorporation of about three interlayer sodium ions in this mica, as discussed in the previous report.[20]

In the estimated chemical formulas of the Ba- and Ca-saturated micas, the total charges of the interlayer cations ($Na^+ + 2\,M^{2+}$) per unit cell are 2.62 and 3.14, respectively, which are close to that of the original Na-3-mica (2.94). The chemical formulas showed that the cation exchange capacities for Ba and Ca ions were 246 and 338 meq $(100\,g)^{-1}$ on anhydrous basis. The CEC for Sr ions was estimated to be 313 meq $(100\,g)^{-1}$ on anhydrous basis in the previous report.[20] The theoretical CEC of Na-2-mica of $Na_2Mg_6Al_2Si_6O_{20}F_4$ is only

Table 1. Metal-oxide contents of the Na-3-mica and Ba-, Ca-, and Mg-saturated Na-3-mica.

Content[a]/wt.%										
Materials	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	Na_2O	CaO	BaO	SrO	H_2O
Mg-saturated Na-3-mica	40.0	12.3	0.66	0.36	33.0	0.79	–	–	–	15.9
Ca-saturated Na-3-mica	38.6	12.2	0.66	0.35	26.2	1.26	8.85	–	–	12.8
Ba-saturated Na-3-mica	37.6	12.0	0.65	0.34	24.6	1.15	–	19.0	–	5.0

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

Table 2. Structural formulas[a] of mica samples.

Mica sample	Chemical composition
Ba-saturated Na-3-mica	$Na_{0.34}Ba_{1.14}(Mg_{5.64}Ti_{0.08}Fe_{0.04})_{oct}(Si_{5.78}Al_{2.18})_{tet}O_{20}F_4 \cdot 2.70H_2O$
Mg-saturatedNa-3-mica[b]	$Na_{0.36}Mg_{1.29}(Mg_{5.78}Ti_{0.07}Fe_{0.04})_{oct}(Si_{5.74}Al_{2.08})_{tet}\ O_{20}F_4 \cdot 8.39H_2O$
Ca-saturated Na-3-mica	$Na_{0.36}Ca_{1.39}(Mg_{5.73}Ti_{0.07}Fe_{0.04})_{oct}(Si_{5.66}Al_{2.11})_{tet}O_{20}F_4 \cdot 6.70H_2O$

[a] The chemical formula was estimated as follows: The mica formula can be represented by,

$$Na_x(Mg_wFe_vTi_u)_{oct}(Si_yAl_z)_{tet}O_{20}F_4$$

First, the atomic proportions were calculated from the metal oxide content in Table 1. These proportions (X, Y, Z, etc., represented by the same letters as those given the above formula) were multiplied by a factor (F) to obtain the actual amounts (x, y, z, etc.) in the formula, for example, $F \times Y = y$. The factor F can be calculated from the charge balance because the total number of positive charges is equal to the total number of negative charges (44 in the $O_{20}F_4$ formula unit).

[b] The number of interlayer Mg ions and octahedral Mg ions were estimated using the following equation:

$$2Mg^{2+}(\text{interlayer}) + Na^{+} = 2.94(\text{total layer charges of original Na-3-mica})$$

$$Mg^{2+}(\text{octahedral sheet}) = Mg^{2+}(\text{total}) - Mg^{2+}(\text{interlayer})$$

$247\,\text{meq}\,(100\,\text{g})^{-1}$ while Na-3-mica is expected to have $357\,\text{meq}\,(100\,\text{g})^{-1}$ based on the estimated chemical composition (anhydrous basis). The Ca and Sr capacities exceeded the theoretical CEC of Na-2-mica. These data indicate that this mica has a larger number of exchangeable sodium ions per unit cell than those expected for Na-2-mica and supports the fact that about three exchangeable sodium ions are located in the interlayers per unit cell. For the Mg-saturated mica, the interlayer Mg ions and octahedral Mg ions could not be distinguished here. Thus, the number of interlayer Mg ions and octahedral Mg ions were estimated using the following equation:

$$\begin{aligned} &2Mg^{2+}(\text{interlayer}) + Na^{+} \\ &\quad = 2.94(\text{total layer charges of original Na-3-mica}) \end{aligned}$$

$$Mg^{2+}(\text{octahedral sheet}) = Mg^{2+}(\text{total}) - Mg^{2+}(\text{interlayer})$$

The estimated chemical formula of Mg-saturated mica was given in Table 2. From this formula, the cation-exchange capacities for Mg is determined to be 322 meq $(100\,g)^{-1}$ on anhydrous basis. These data show that about 80% to 90% of the Na ions in the Na-3-mica is exchangeable for alkaline earth metal ions of Mg, Ca, Sr, and Ba.

The XRD patterns of the original Na-3-mica and Ba-, Mg-, and Ca-saturated micas are shown in Fig. 1. In the XRD pattern of the original mica (Fig. 1a), a strong peak was observed at $d = 12.10$ Å, which can be assigned to the (001) reflection of hydrated mica with a single sheet of interlayer water.[9] Small peaks at $d = 6.09$, 4.05, and 3.04 are assigned to (002), (003), and (004) reflections of c-axis spacing of the hydrated mica. This narrow interlayer spacing of about 2 Å indicates that the interlayer Na^+ ions are accommodated in the ditrigonal holes on the silicate layers above and below the central single sheet of interlayer water.[9] The interlayer cations probably occupy a less-perfect octahedral environment consisting of three interlayer water molecules and three oxygens of the silicate layer surface.

The XRD pattern of the Sr-saturated mica was given in the previous report,[20] which showed only the peaks due to hydrated mica with the basal spacing of $d = 12.19$ Å [See Fig. 2a in Ref.[20]]. It showed that the Sr-saturated mica retained the hydrated interlayer structure of Na-3-mica and Sr ions were also accommodated in the ditrigonal holes above and below the central single water sheet in the interlayer spacings.

In the XRD pattern of the Ba-saturated mica (Fig. 1b), any peaks due to the hydrated mica were not observed. The peak at $d = 10.04$ Å appeared, which can be assigned to the (001) reflection of anhydrous mica, indicating the collapse of interlayers. This collapse is caused by the incorporation of a large number of less hydrated Ba ions in the interlayers. The hydration enthalpy of the alkaline earth metal ion ($-\Delta H^{\circ}_{\text{hydration}}$) increases in order of Ba < Sr < Ca < Mg. Thus, the degree of the hydration of cation increases in this order.

In the XRD pattern of the Mg-saturated mica, a mixture of two swelling phases is observed. One showed the (001) reflection peak at $d = 13.69$ Å and another at $d = 14.47$ Å (Fig. 1c). In the hydrated interlayer structure of the 13.69-Å phase, the interlayer cations are accommodated in the ditrigonal holes on the silicate layers above and below the central double sheets of interlayer water.[9,21] In the 14.47-Å phase, the interlayer cations occupy the octahedral coordination between two sheets of hexagonal water-molecule network, which are midway between the silicate layers. Normally, such a hydrated interlayer structure occurs in wide interlayer spacings of about 4 to 5 Å of swelling 2:1 phyllosilicate clays.[21] The hydrated interlayer structure is

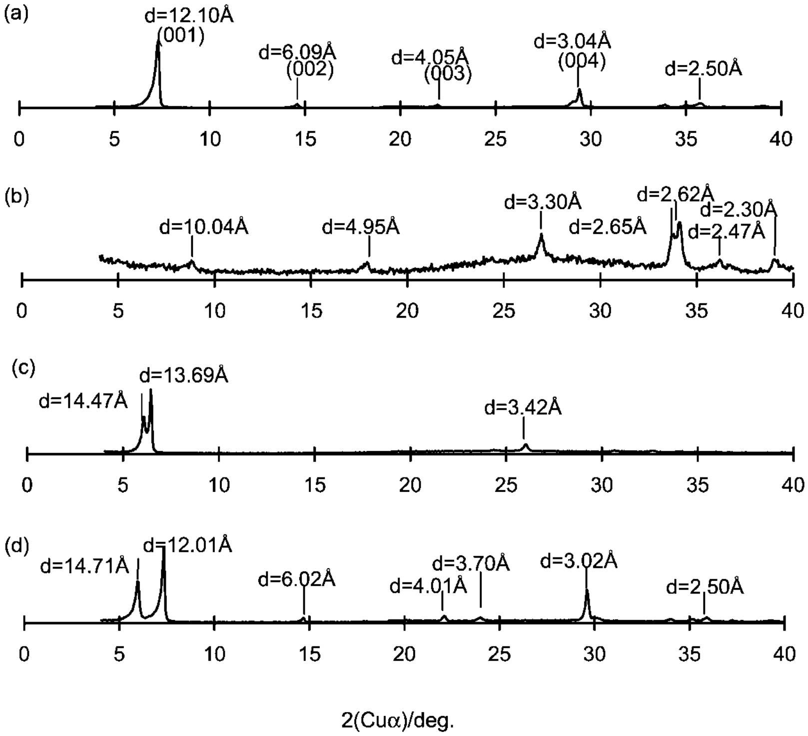

Figure 1. X-ray diffraction patterns of (a) the original Na-3-mica, (b) Ba-, (c) Mg-, and (d) Ca-saturated Na-3-mica.

influenced by the nature of interlayer cation and its concentration, and also by the layer-charge density of the silicate layer.[21] The presence of two swelling mica phases with different hydrated interlayer structures in the Mg-saturated mica is considered due to the fact that the Na-3-mica had a nonuniform distribution of chemical composition of the silicate layers or a nonuniform distribution of the layer-charge densities of the silicate layers, which can be caused by the nonuniform distribution of Mg vacancies in octahedral sites and/or of Al ions in tetrahedral sites in the layers. Normally, a lower-layer-charged phase of the 2:1 phyllosilicate expands its interlayer to a larger extent. As indicated by Fig. 1c, the strong hydration of the interlayer Mg ions expanded the mica structure largely to yield 13.69-Å and 14.47-Å phases. Thus, the partial phase of the Na-3-mica, having relatively low-layer-charge densities, or the relatively Na-poor phase, is considered to expand to a larger extent after Mg^{2+}/Na^{+} exchange. The largely expanded 14.47-Å phase would occur from the partial Na-poor phase in the Na-3-mica while the partial phase with the relatively high-layer-charge densities, or the relatively Na-rich phase would be transformed into the 13.69-Å phase. This idea is shown schematically in Fig. 2.

The Ca-saturated mica also gave two types of phases due to the strong hydration of interlayer Ca ions. One showed the (001) reflection peak at d = 12.01 Å and another at d = 14.71 Å (Fig. 1d). It is considered that the relatively Na-rich region in Na-3-mica was transformed into the 12.01-Å phase while the 14.71-Å phase occurred from the relatively Na-poor region. As discussed below, the amount of Ca^{2+} ions incorporated in the Na-rich region would be relatively small to be less than 37% of Ca ions in the Ca-saturated mica. In this Na-rich region, although Ca^{2+} ion has the relatively large hydration enthalpy, the hydrated interlayer structure (12-Å phase) was not expanded. The interlayer spacing of about 2 Å indicates that the interlayer Ca^{2+} ions were accommodated in the ditrigonal holes on the silicate layers above and below the central single sheet of interlayer water, as similar to interlayer Na^+ ions in the Na-3-mica. This will be due to the low concentration of Ca^{2+} in the interlayers. The 12-Å lattice phase of the Ca-saturated mica was rather slightly shrunk to d = 12.01 Å in comparison to that of the original Na-3-mica (d = 12.10 Å). This will be because the divalent ion of Ca^{2+} is more strongly and deeply trapped, by Coulombic forces, in the ditrigonal holes on the silicate layers than the univalent Na^+ ion in this case the effective ionic radii (EIR) of Ca^{2+} and Na^+ are almost the same value of 114–116 pm.

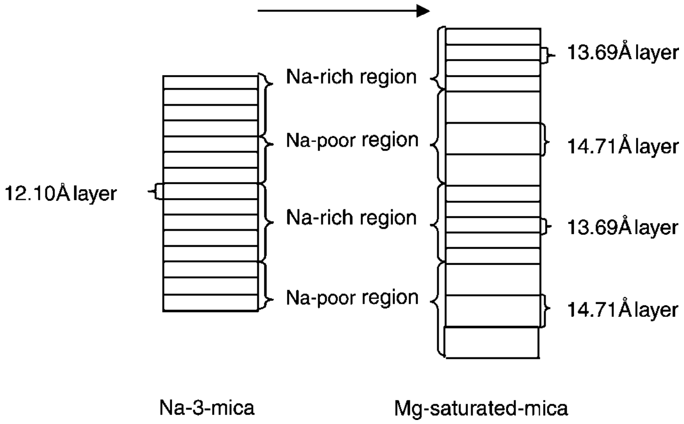

Figure 2. Schematic of changes in the interlayer spacings of Na-3-mica by the Mg^{2+}/Na^+ exchange.

As mentioned above, in the case of the Sr-saturated mica, the 12-Å lattice phase was slightly expanded to d = 12.19 Å. This will be because the EIR of Sr^{2+} (132 pm) is significantly larger than that of Na^+. Furthermore, in this case, all of the Sr^{2+} ions in the Sr-saturated mica were incorporated only in the 12-Å lattices (a single phase of 12.19-Å phase was formed in the Sr-saturated mica) and, thus, the Sr^{2+} concentration was high. On the other hand, for the Na-poor region, the amount of Ca^{2+} incorporated would be more than 63%, as discussed below. Because of the high Ca^{2+} concentration in the interlayers and the low-layer-charge densities, the hydrated interlayer structure of the Na-poor region drastically changed and the expanded 14-Å lattices were created by the relatively strong hydration of Ca^{2+}.

In summary, Sr^{2+} ions with the relatively small hydration enthalpy do not expand in the both of the Na-rich and Na-poor regions and the mica phase retains the 12-Å lattices. Ba^{2+} has a very small hydration enthalpy and then the interlayers collapse. In the case of Ca^{2+} with a relatively large hydration enthalpy, when Ca-saturated, the large portion of Ca^{2+} ions are incorporated in the Na-poor region and this region is expanded to the 14-Å lattices because of the high Ca^{2+} concentration. However, when the Ca^{2+} concentration is low in interlayers, the Ca^{2+} ions cannot expand the Na-poor region. In this case, the Ca^{2+} ions rather slightly shrink the 12-Å lattifces, forming the 12.01-Å lattice phase, as shown in Fig. 4c. With Mg^{2+} with a very large hydration enthalpy, the Na-poor and Na-rich regions are both expanded and spitted into the 14-Å and 13-Å lattices when Mg-saturated.

The metal leaching tests were carried out using the M-saturated micas in a 0.5 M NaCl background solution at room temperature. Figure 3 shows time variations of released amounts of M ions from the M-saturated micas and the result of the Sr leaching test, which had been done in our previous paper,[20] was also shown here for comparison. These data indicate that the degree of immobilization of alkaline earth metals in the interlayers of Na-3-mica increases in the order of Ca < Sr < Ba < Mg.

Only 20% of the Ba ions in Ba-saturated mica were released to the solution phase. In the Ba-saturated mica, the collapse of interlayer spacings was observed because of less hydration of Ba ion. In this case, the interlayer cations are strongly fixed in the interlayers because they are sandwiched between the ditrigonal holes of silicate layers above and below. There are no significant changes between the XRD patterns before and after the Ba leaching test (Fig. 1b and Fig 4a).

For Sr ions, which are more hydrated than Ba ions, the Sr-saturated mica retained the hydrated 12.19-Å phase.[20] However, about 30% of the Sr ions in the Sr-saturated mica were released to the solution and about 70% Sr ions were trapped in the interlayers. As mentioned above, in the 12-Å phase, the interlayer

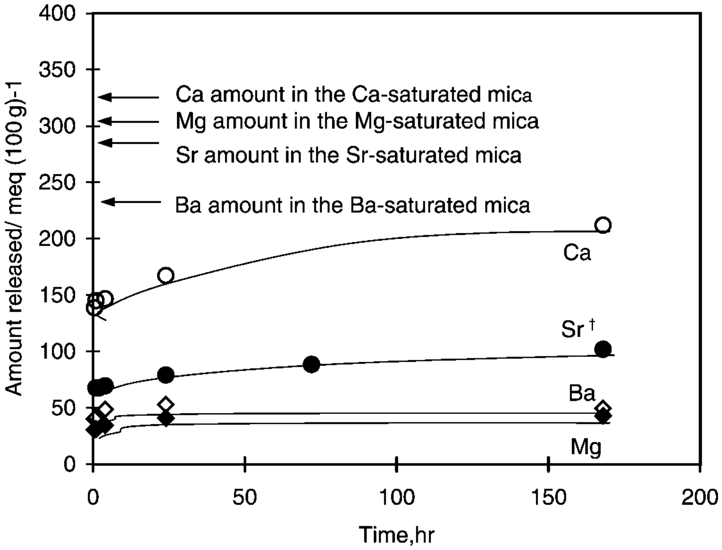

Figure 3. Time variations of released amounts of M ions from the M-saturated Na-3-micas; M = Ca, Sr, Ba, and Mg. †The date for Sr was taken from Ref.[20].

cations coordinate with the ditrigonal holes of silicate layers, having a less-perfect octahedral environment consisting of three interlayer water molecules and three oxygens of the silicate layer surface. In this case, divalent Sr ions are trapped by the strong Coulombic forces in the ditrigonal holes of the highly charged silicate layers.

Only 13% of Mg ions were released from the Mg-saturated mica, but its XRD pattern drastically changed before and after the leaching test. After the leaching test, the 14.47-Å phase disappeared and the 12.35-Å phase appeared; in addition, a reflection peak of 13.69 Å slightly shifted to 13.58 Å (Fig. 1c and Fig. 4b). It is considered that the Mg^{2+} ions were mostly incorporated in the 13-Å phase and that a small portion of Mg^{2+} was incorporated in the 14-Å phase in the Mg-saturated mica. The Mg release (13%) would occur mainly from the 14-Å phase of the Mg-saturated mica, resulting in formation of the 12.35-Å phase. Normally, interlayer cations in 14- and 15-Å phases are readily exchangeable because they are located midway in between the silicate layers and are coordinated with water-molecule sheets above and below the cations.[21] On the other hand, in 13-Å phases, the interlayer cations still coordinate with the ditrigonal holes of silicate layers, as described above. Because of the strong Coulombic forces between the divalent ion and

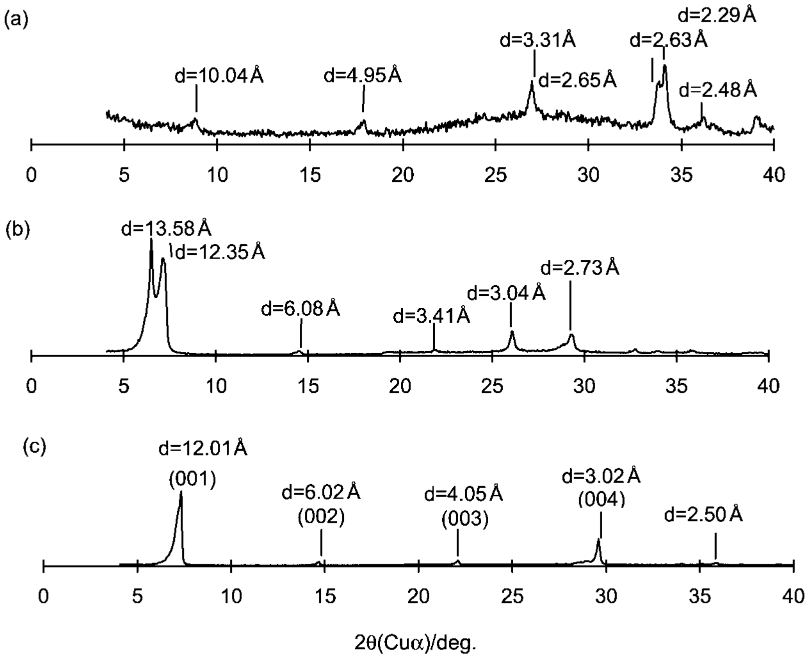

Figure 4. X-ray diffraction patterns of the (a) Ba-, (b) Mg-, and (c) Ca-saturated Na-3-micas after the leaching tests in 0.5 M NaCl background solutions at room temperature.

the highly charged layer, most of the Mg ions in this 13-Å phase would be trapped in the interlayers.

Sixty three percent of Ca ions could be released from the Ca-saturated mica. After the release of Ca ions, the 14.71-Å phase disappeared and a single phase of d = 12.01 Å was formed (Fig. 1d and Fig. 4c). Thus, the Ca release is considered to occur from the 14.71-Å phase. Before Ca releasing, a large portion of Ca ions (more than 63%) would be incorporated in the 14.71-Å phase that had a relatively low-layer-charge density. The rest (less than 37%) would be incorporated in the 12.01-Å phase that had the high-layer-charge density. After releasing a part of Ca ions from the 14.71-Å phase (63%), an apparently stable single 12.01-Å phase was formed throughout the whole mica phase. This 12.01-Å phase had still 37% of Ca^{2+} ions in the interlayers. The interlayer spacings of the 12-Å lattices was slightly narrower than that of the pure Na-form mica because the divalent Ca^{2+} ion is more deeply trapped in the ditrigonal holes on the silicate layers than the univalent Na^+ ion as discussed above.

CONCLUSION

The cation-exchange capacities of Na-3-mica are 338, 322, and 246 meq $(100\,g)^{-1}$ for the alkaline metals of Ca, Mg, and Ba, respectively, on the anhydrous basis of this mica phase. About 80% to 90% of the Na ions in the Na-3-mica are exchangeable with these alkaline earth-metal cations. In the metal-cation leaching tests, 80%, 87%, and 37% of the exchanged Ba, Mg, and Ca ions, respectively, were found to be immobilized. These bivalent ions appear to be fixed in the 10.0–13.6 Å phases because, in their interlayer structures, the interlayer cations coordinate directly with the ditrigonal holes of silicate layers, having a less-perfect octahedral environment consisting of three interlayer water molecules and three oxygens of the silicate layer surface. Due to the strong Coulombic forces between the divalent ion and the highly charged silicate layer, the alkaline earth metal ions are apparently trapped in the interlayers. On the contrary, the interlayer cations in the 14-Å phase are very exchangeable and readily released to the solution phase from the interlayers because the interlayer cations coordinate not with the silicate layer, but only with water-molecule sheets above and below the cations.

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