

# Na-4-mica: simplified synthesis from kaolinite, characterization and Zn, Cd, Pb, Cu and Ba uptake kinetics

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A swelling Na-4-mica of the brittle mica type (ideal chemical composition of  $\text{Na}_4\text{Mg}_6\text{Al}_4\text{Si}_4\text{O}_{20}\text{F}_4 \cdot x\text{H}_2\text{O}$ ) was prepared by a simplified one-step synthetic process from kaolinite at or below 800 °C. Hydrated and well-dispersed Na-4-mica particles of about 2 µm in size were prepared at 800 °C. The <sup>27</sup>Al MAS-NMR spectrum of this mica showed that almost all Al was in tetrahedral coordination while the <sup>29</sup>Si MAS-NMR spectrum showed that the nearest neighbor environment of Si was mainly Si(3Al), as expected based on the Si:Al molar ratio of 1:1 in the Na-4-mica. The CEC of the mica was determined to be 447 mequiv (100 g)<sup>-1</sup>. With this Na-4-mica, the Zn, Cd, Pb, Cu and Ba uptake kinetics were investigated in a 0.5 M NaCl background solution at room temperature and were found to be quite rapid.

## Introduction

Naturally occurring and synthetic clays and zeolites are well known groups of inorganic cation exchangers. Mica is one of the most representative of the 2:1 phyllosilicate clays, each layer consisting of an octahedral sheet sandwiched between two tetrahedral sheets. Micaceous clays have the highest layer charge density among the clays and there are two main categories of micas based on layer charge density: 1) true micas with 1 negative charge per formula unit and 2) brittle micas with 2 negative charges per formula unit.<sup>1</sup> Although the naturally occurring micas are of the non-swelling type, synthetic micas which swell in water can be prepared by hydrothermal, solid-state and topotactic exchange methods.<sup>2–5</sup> However, all the synthetic swelling micas prepared to date are of the true mica type except for one which is of the brittle mica type and was named Na-4-mica.<sup>6–14</sup>

The ideal chemical composition of Na-4-mica is  $\text{Na}_4\text{Mg}_6\text{Al}_4\text{Si}_4\text{O}_{20}\text{F}_4 \cdot x\text{H}_2\text{O}$  and it has a theoretical cation-exchange capacity (CEC) of 468 mequiv (100 g)<sup>-1</sup> on an anhydrous basis. In spite of the high-layer-charge density, it can readily swell on contact with water or even in moist air at ambient conditions.<sup>6–14</sup> Na-4-mica contains an unusually large number of 4 interlayer cations per unit cell. The presence of this unusually large number of interlayer cations and a resulting offset layer stacking by 1/3 'b', allows the structure to expand from a dehydrated 9.81 Å to a hydrated 12.18 Å c-axis spacing to achieve a more thermodynamically stable interlayer structure.

Gregorkiewicz *et al.*<sup>6</sup> first synthesized this special mica as millimeter sized flakes by reacting natural augite crystals in a 1:1 molar ratio NaF–MgF<sub>2</sub> melt at approximately 900 °C. One of the present authors previously reported that a very fine and pure phase of Na-4-mica, which is essential for practical applications, could be prepared by a solution–sol–gel process using tetraethylorthosilicate (TEOS), aluminium and magnesium nitrates.<sup>8,9</sup> A simplified procedure was later developed for

the synthesis of this mica using fumed silica instead of TEOS as the silica source.<sup>10</sup> Recently, we have been able to easily and economically synthesize Na-4-mica at 850–890 °C from a mixture of NaF, ultrafine MgO and calcined kaolinite (metakaolin), the latter serving as a cost-effective aluminosilicate source with the desired 1:1 Si to Al molar ratio.<sup>11</sup> This mica was very selective for the hazardous divalent transition metals Cd, Zn, Pb and Cu, and the alkaline earth metal Ba when the metal loading in the mica was relatively low (fractional exchange in mica  $\bar{X}_M < 0.1–0.4$ ).<sup>12–14</sup> The cation-exchange capacities for these cations were also large, ranging from 117 to 295 mequiv (100 g)<sup>-1</sup>, even at very low metal concentrations of  $2.3–3.5 \times 10^{-3}$  M solution.

In the present work, we further simplified the synthesis of the Na-4-micas by a one-step process from kaolinite and magnesium nitrate using NaF flux below 800 °C, and characterized them by XRD, SEM and <sup>27</sup>Al and <sup>29</sup>Si magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. Furthermore, with the fine and well-dispersed Na-4-mica crystals prepared, Cd, Pb, Cu and Ba uptake kinetics were studied.

## Experimental

### Preparation of Na-4-micas

Na-4-mica was previously prepared from a mixture of ultrafine MgO (supplied by Ube Industries, Ube, Japan), NaF and calcined kaolinite (metakaolin) at 850–890 °C.<sup>11–14</sup> Naturally occurring kaolinite has the theoretical chemical composition  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ : the poorly crystallized kaolinite of composition 47.9% SiO<sub>2</sub>, 38.3% Al<sub>2</sub>O<sub>3</sub>, 2.08% TiO<sub>2</sub>, 0.98% Fe<sub>2</sub>O<sub>3</sub>, 0.15% FeO and 0.03% MgO (supplied by Georgia Kaolin Company though W.D. Johns, Dept. of Geology, Univ. of Missouri, Columbia, MO 65201, USA), was used for the synthesis of all the Na-4-micas. The previous or original synthetic process of Na-4-mica is briefly outlined as follows:<sup>11</sup> the kaolinite was first calcined at 700 °C for 18 h to transform it to an amorphous product (on heating to around 600 °C, kaolinite is completely dehydrated and loses its crystalline character), the so-called metakaolin (Al<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>). Appropriate

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amounts of ultrafine MgO and metakaolin were mixed to obtain a stoichiometric composition. Then it was mixed with an equal mass of NaF, thoroughly homogenized using a pestle and mortar, and transferred to a platinum vessel. The precursor mixture was calcined for 24 h at 850–890 °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.<sup>11</sup> Then, the solid was washed with 1 M NaCl solution three times to completely saturate all the exchange sites with Na<sup>+</sup>. The product was finally washed with deionized water and dried at 60 °C in an oven for 2–3 days. The products thus prepared were stored in a desiccator over silica gel at room temperature.

In the present work, the synthetic procedure was simplified as follows. Poorly crystallized kaolinite was directly used for the preparation of the precursor mixture. In addition, magnesium nitrate was used as the magnesium source instead of ultrafine MgO in order to reduce the reaction temperature during synthesis: magnesium nitrate is expected to be more reactive than MgO and favor the low temperature formation of Na-4-mica because of melting of Mg(NO<sub>3</sub>)<sub>2</sub> at low temperatures which probably led to better homogenization. Stoichiometric quantities of the kaolinite and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were mixed with an equal mass of NaF and homogenized. The water content of the kaolinite was previously determined to be 14.16 wt% by thermal analysis using a TG DTA 2010, Mac Science. The precursor mixture was calcined directly at 700, 750 and 800 °C. The resulting solids were washed, dried and stored in the same way as in the original procedure.

### Characterization of products

Powder X-ray diffraction (XRD) was carried out to check for phase purity and to determine the basal spacings of the Na-4-mica using a Rigaku RAD-γA diffractometer with CuKα radiation. Scanning electron microscopy (SEM) was used to determine particle size and shape (EPMA-8705, Shimadzu). The water content of the hydrated Na-4-mica was determined by thermal analysis. Magnetic-angle spinning NMR <sup>27</sup>Al and <sup>29</sup>Si spectra were obtained at 103.9 and 79.8 MHz respectively using a Varion Unity 400 spectrometer with a double bearing rotor (5 mm, Zirconia).<sup>15</sup> For <sup>27</sup>Al resonance the spectrometer operating conditions were: pulse width 1 μs (equivalent to a π/18 pulse, measured on Al(NO<sub>3</sub>)<sub>3</sub> aqueous solution), spectral width 1 MHz, recycle delay 1.0 s, number of transients 2000, and spinning speed 12 kHz. No line broadening was considered in the data processing.<sup>15</sup> Chemical shifts were measured relative to aqueous Al(NO<sub>3</sub>)<sub>3</sub>. The <sup>29</sup>Si spectra were acquired by using a 4 μs pulse width, 40 kHz spectral width, recycle delay of 60 s, 1000 transients, and 8 kHz spinning speed.<sup>15</sup> Line broadening of 10 Hz was used in the data processing. Chemical shifts were referenced to the signal of tetramethylsilane (TMS).

### CEC determination of Na-4-mica

About 50 mg of the Na-4-mica sample was placed in a clean and weighed glass centrifuge tube. The centrifuge tube containing the sample was weighed to determine the exact weight of the sample. The sample was washed three times with 10 cm<sup>3</sup> of 0.5 M NaCl solution to completely saturate all the exchangeable sites in the mica with Na<sup>+</sup>, and then washed five times with 10 cm<sup>3</sup> of 0.01 M NaCl solution. After weighing the centrifuge tube, Na<sup>+</sup> ions in the mica were replaced with K<sup>+</sup> by five washings with 10 cm<sup>3</sup> of 0.5 M KCl solution and the washings were collected in a 100 cm<sup>3</sup> volumetric flask. The flask was filled up to 100 cm<sup>3</sup> with 0.5 M KCl solution. The released amount of Na<sup>+</sup> ions was determined by atomic emission spectroscopy (SpectraSpan III instrument) and a correction

was made for residual 0.01 M NaCl solution from weighing. Three replicates were used for each duration to check for reproducibility. The errors in the triplicates were about ± 2%.

### Zn, Cd, Pb, Cu and Ba uptake kinetics study

Cation uptake kinetics from 0.5 M NaCl background solution were determined for Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Ba<sup>2+</sup> in a batch experiment using the Na<sup>+</sup>-saturated Na-4-mica which had been prepared at 800 °C. 20 mg of mica sample (anhydrous basis) was added to 25 cm<sup>3</sup> of 0.5 M NaCl containing 0.0001 M MCl<sub>2</sub> (M = Zn, Cd, Pb, Cu and Ba) in polypropylene centrifuge tubes. The centrifuge tubes were agitated continuously on a reciprocating shaker at room temperature for 1, 2, 5 and 30 min and for 2 h, 8 h, 1 day, 1 week and 4 weeks. Then, the solid and solution phases were separated by a filter syringe (for 1, 2, 5 and 30 min) or by centrifugation (for 2 h, 8 h, 1 day, 1 week and 4 weeks). The solutions were analyzed for M<sup>2+</sup> remaining in solution by atomic emission spectroscopy. Three replicates were used for each duration to check for reproducibility. The errors in the triplicates were about ± 5%.

The modified Freundlich kinetic model given below was used to describe the 2Na<sup>+</sup> → M<sup>2+</sup> exchange by the Na-4-mica. The modified Freundlich model as proposed by Kuo and Lotse<sup>16</sup> has been successfully applied to experimental data on ion exchange or adsorption with soils and clays by many researchers:

$$M_t = kC_0 t^{1/m} \quad (1)$$

or

$$\log_{10} M_t = (\log_{10} k + \log_{10} C_0) + 1/m \log_{10} t \quad (2)$$

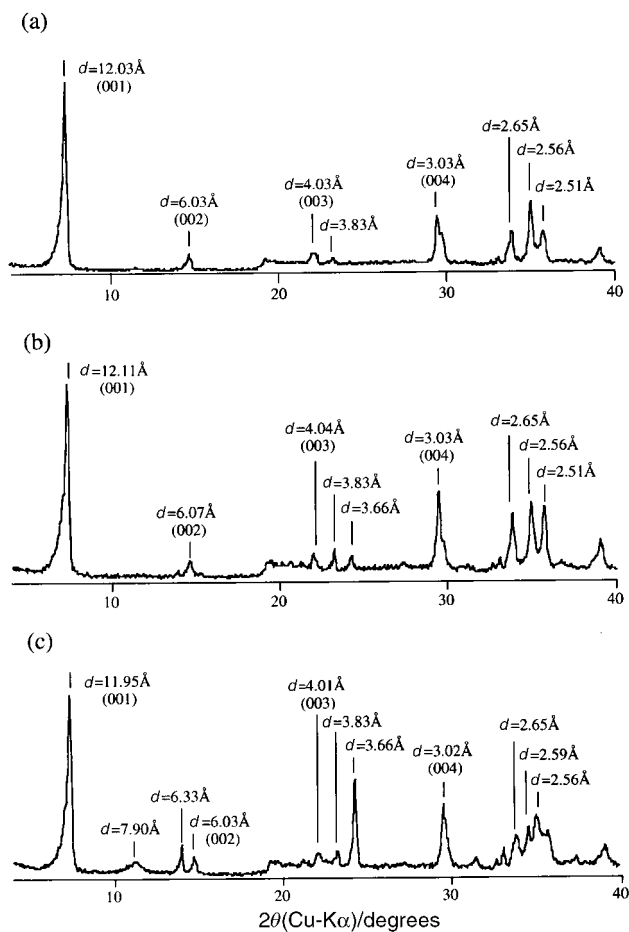
where  $M_t$  is the amount of M<sup>2+</sup> adsorbed on the mica (mmol g<sup>-1</sup>) at time  $t$ ,  $k$  is the rate coefficient,  $C_0$  is the initial M<sup>2+</sup> concentration and  $m$  is a constant. A plot of  $\log_{10} M_t$  vs.  $\log_{10} t$  should be linear if the M<sup>2+</sup> exchange conforms to the modified Freundlich model. The goodness of conformity between experimental data and the model-predicted values was expressed by the coefficient of determination ( $r^2$ ). A relatively high  $r^2$  value for the relationship between measured and predicted cation uptake data indicates that the model successfully described the kinetics of 2Na<sup>+</sup> → M<sup>2+</sup> exchange by the Na-4-mica.

## Results and discussion

### Characterization of Na-4-mica

In the XRD pattern of the resultant solid prepared at 800 °C (Fig. 1a), a strong peak for the (001) reflection of the hydrated Na-4-mica with a single sheet of interlayer water was observed at  $d = 12.03$  Å. Small peaks observed around  $d = 6.03$ , 4.03 and 3.03 Å are assigned to the (002), (003) and (004) reflections of  $c$ -axis spacing of the hydrated Na-4-mica. Other small peaks were almost consistent with the limited powder XRD data reported previously for the hydrated Na-4-mica.<sup>9–11,16</sup> The strong peaks of the hydrated Na-4-mica were also observed in the XRD pattern of the solid prepared at 750 °C but a small and unknown peak appeared at  $d = 3.66$  Å (Fig. 1b). In the XRD pattern of the solid prepared at 700 °C (Fig. 1c), the unknown peak at  $d = 3.66$  Å became more intense. The unknown peaks for the impurity phase also appeared at  $d = 7.90$  and 6.33 Å.

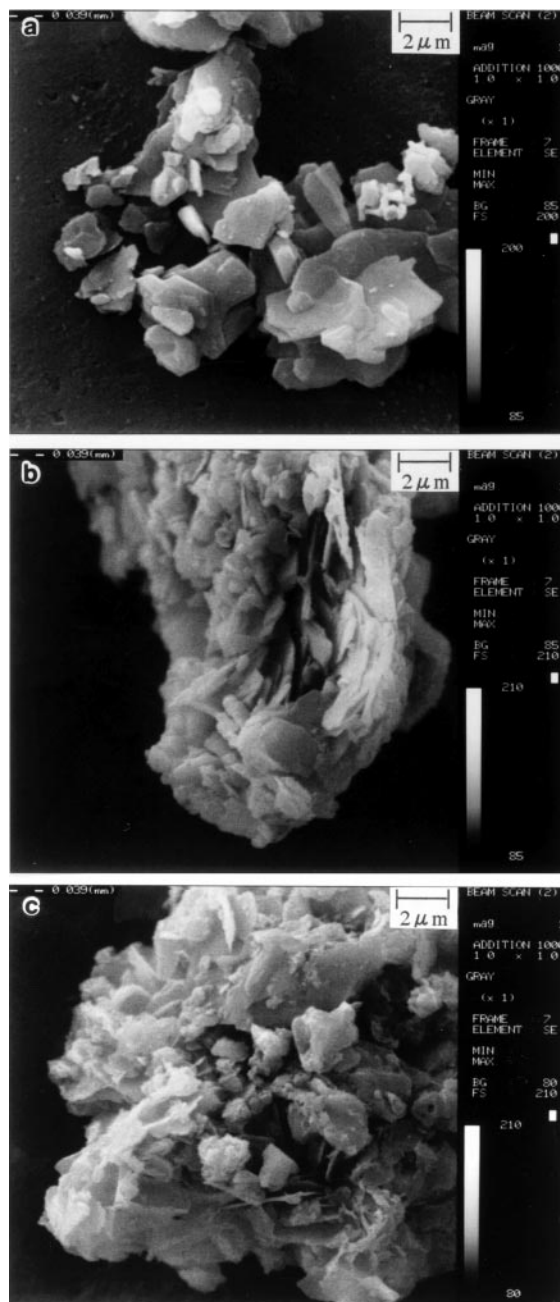
The SEM micrograph of the mica prepared at 800 °C showed the plate-like and pseudo hexagonal crystallites (Fig. 2a). The mica had a size distribution between 0.4 and 4 μm and most of the crystallites were about 2 μm. For the mica prepared at 750 °C, the crystallites were plate-like but the hexagonal shapes were not clearly observed (Fig. 2b). At 700 °C, undifferentiated plate-like particles were formed (Fig. 2c). In the mica samples



**Fig. 1** XRD patterns of Na-4-mica samples prepared by the simplified synthetic process from the mixture of kaolinite, magnesium nitrate and NaF at (a) 800, (b) 750 and (c) 700 °C.

prepared at 700 and 750 °C, almost all of the plate-like crystallites agglomerated to form massive grains.

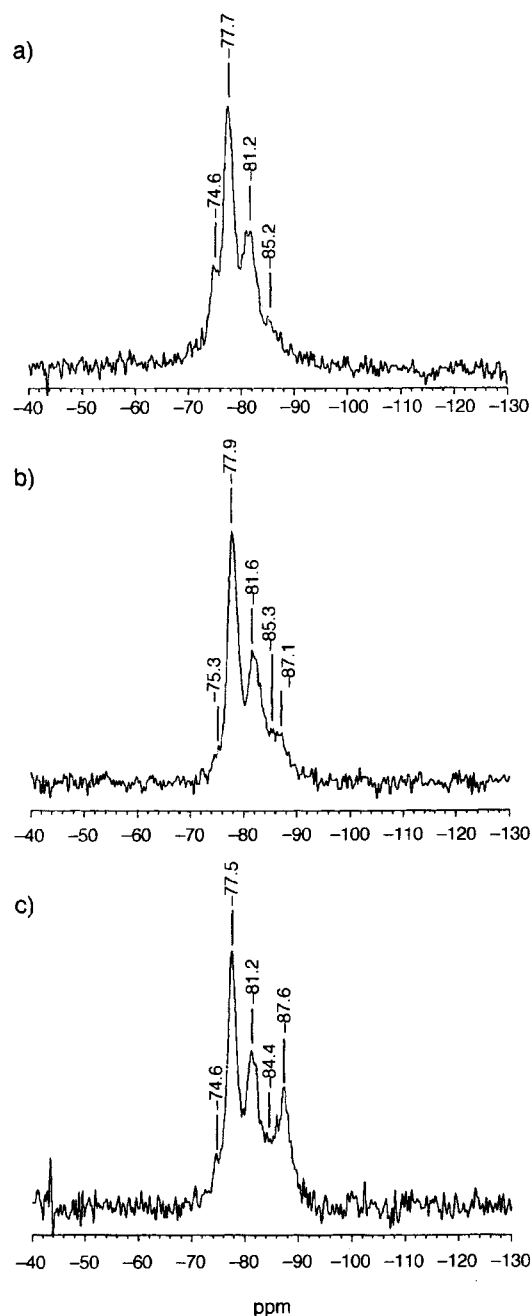
The  $^{29}\text{Si}$  MAS-NMR spectra are presented in Fig. 3. A complete Si/Al ordering in the Na-4-mica of ideal composition would give only one resonance due to the Si(3Al) environment. These spectra, however, showed the presence of two Si(3Al) resonances at  $\delta$  -78 and -75 ppm, which represent two types of these environments. For the hydrated Na-4-micas which had been prepared before, the resonance for Si(3Al) predominantly appeared around  $\delta$  -78 ppm.<sup>9,11,15,17</sup> Frequently, however, the small Si(3Al) resonance was also observed around  $\delta$  -75 ppm.<sup>11,15</sup> Slight changes in the chemical shifts of resonances corresponding to the same tetrahedral environment have been previously attributed to differences in the octahedral and interlayer environment of silicon.<sup>17</sup> Komarneni *et al.* suggested that the resonance around  $\delta$  -75 ppm may be due to the Si(3Al) of the anhydrous Na-4-mica phase because the completely anhydrous mica prepared by the solution-sol-gel process at 850 °C showed predominantly a resonance at  $\delta$  -74.7 ppm with a minor resonance at -78.3 ppm.<sup>16</sup> These micas prepared here may contain a very small portion of anhydrous phase or poorly hydrated phase, although it was not detected by the XRD analyses (Fig. 1). All the micas synthesized here showed significant resonances at 81–82 and 84–85 ppm. The former can be assigned to Si(2Al) and the latter to Si(1Al), respectively, based on previously reported assignments.<sup>11,15,17,18</sup> In the spectra of the samples prepared at 700 and 750 °C, a resonance around  $\delta$  -87 ppm was observed. This resonance might be due to the Si surrounded by three Si. Herrero *et al.*<sup>17</sup> observed a very weak resonance at -88 ppm for the synthesized mica having a chemical composition close



**Fig. 2** SEM micrographs of Na-4-mica samples prepared by the simplified synthetic process from the mixture of kaolinite, magnesium nitrate and NaF at (a) 800, (b) 750 and (c) 700 °C.

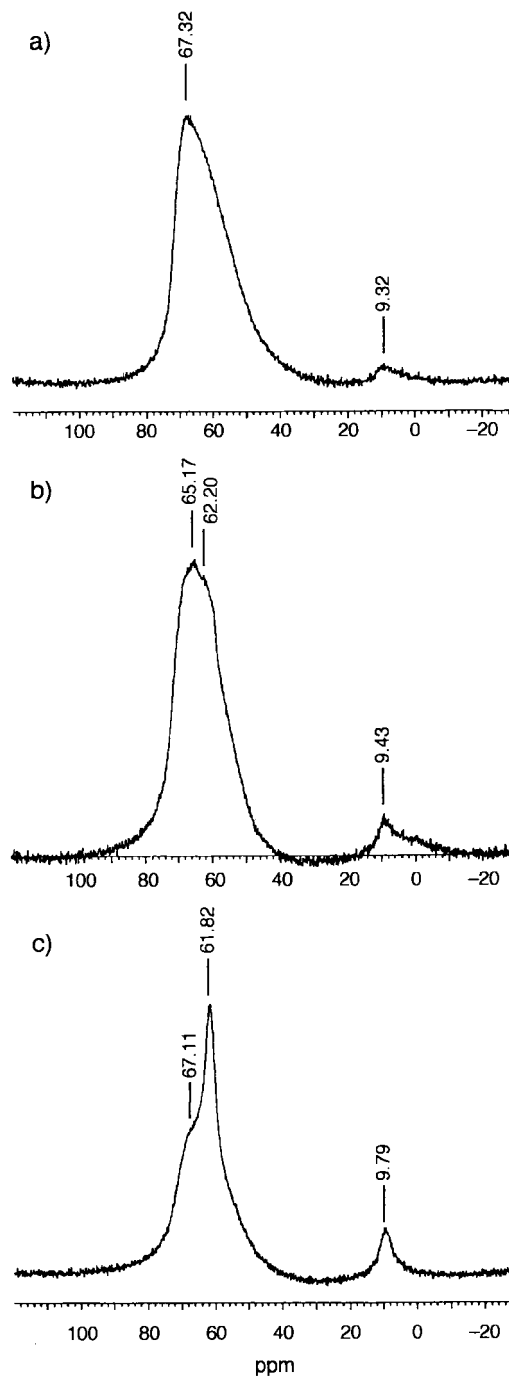
to that of Na-4-mica and assigned it to Si(3Si). However another possibility is that this resonance is due to another Si(1Al) environment. Clay minerals such as phlogopite and vermiculite give a resonance due to the Si(1Al) environment at 86–88 ppm.<sup>18</sup> Table 1 shows the chemical shifts  $\delta$  and the normalized intensities. The  $^{29}\text{Si}$  MAS-NMR data for the Na-4-mica prepared at 800 °C showed that the nearest neighbor environment of Si was mainly Si(Al): 65% of the environment of Si was determined to be Si(3Al). As the calcination temperature decreased, the proportion of Si(3Al) environment decreased.

$^{27}\text{Al}$  MAS-NMR spectra of the mica samples prepared at 700–800 °C are shown in Fig. 4. The spectrum of the mica prepared at 800 °C showed a strong resonance due to the Al in tetrahedral coordination at  $\delta$  ca. 67.3 ppm from  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ . A very small resonance at  $\delta$  9.3 ppm can be assigned to octahedral Al. Thus, the spectrum of the Na-4-mica prepared at 800 °C showed that some Al was incorporated in the



**Fig. 3**  $^{29}\text{Si}$  MAS-NMR spectra (ref. TMS) of Na-4-mica samples prepared by the simplified synthetic process from a mixture of kaolinite, magnesium nitrate and NaF at (a) 800, (b) 750 and (c) 700 °C.

tetrahedral sites. In the spectra of the micas prepared at 700 and 750 °C, a significant resonance at 62 ppm was observed along with the resonances at 67 and 9 ppm, which represented a second Al tetrahedral environment. As the calcination



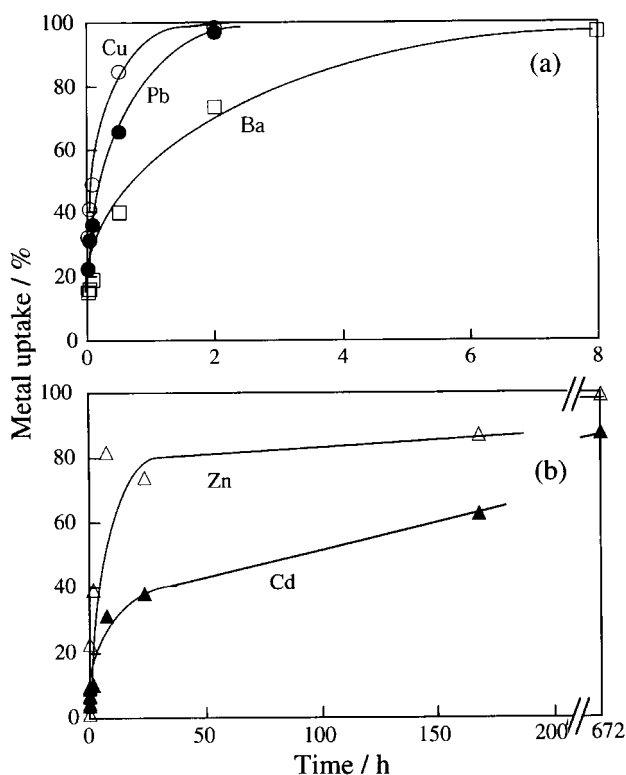
**Fig. 4**  $^{27}\text{Al}$  MAS-NMR spectra (ref.  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ) of Na-4-mica samples prepared by the simplified synthetic process from a mixture of kaolinite, magnesium nitrate and NaF at (a) 800, (b) 750 and (c) 700 °C.

temperature was lower, the resonance around 62 ppm became more intense. It is not clear at this point what this tetrahedral environment is.

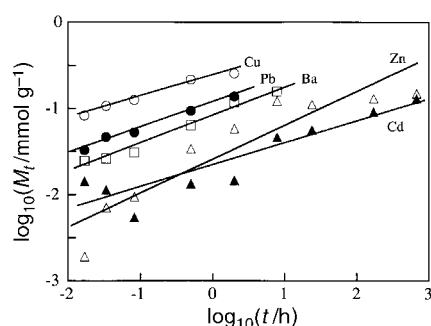
**Table 1**  $^{29}\text{Si}$  MAS-NMR data (chemical shift  $\delta$  relative to TMS and the normalized intensity  $I$ ) for Na-4-mica

| Mica samples | Calcination temperature/°C | Tetrahedral environments of Si <sup>a</sup> |              |              |              |
|--------------|----------------------------|---|--------------|--------------|--------------|
|              |                            | Si(3Al)                                     | Si(2Al)      | Si(1Al)      | Si(1Al)?     |
| Mica-1       | 800                        | $\delta$ : 74.6, 77.7<br>$I$ (%): 64.9      | 81.2<br>25.0 | 85.4<br>10.1 | —<br>—       |
| Mica-2       | 750                        | $\delta$ : 75.3, 77.9<br>$I$ (%): 52.0      | 81.6<br>24.0 | 85.3<br>12.5 | 87.1<br>11.5 |
| Mica-3       | 700                        | $\delta$ : 74.6, 77.5<br>$I$ (%): 45.6      | 81.2<br>23.0 | 84.4<br>13.0 | 87.6<br>18.4 |

<sup>a</sup>Assignment of the chemical shifts was based on refs. 11, 15, 17 and 18.



**Fig. 5** Metal ion uptake kinetics from a 0.5 M NaCl containing 0.0001 M metal chloride by the Na-4-mica prepared by the simplified synthetic process at 800 °C. (a) Cu<sup>2+</sup> (○), Pb<sup>2+</sup> (●) and Ba<sup>2+</sup> (□), and (b) Zn<sup>2+</sup> (△) and Cd<sup>2+</sup> (▲).



**Fig. 6** Relationship between M<sup>2+</sup> exchanged with time as described by the modified Freundlich model. Cu<sup>2+</sup> (○), Pb<sup>2+</sup> (●), Ba<sup>2+</sup> (□), Zn<sup>2+</sup> (△) and Cd<sup>2+</sup> (▲).

These characterizations showed that the purest and well-dispersed phase of hydrated Na-4-mica in the crystallite size of about 2 μm was prepared at 800 °C. We used this Na-4-mica sample for the cation exchange kinetic studies.

### Cation exchange kinetics

The CEC of the Na-4-mica prepared at 800 °C was determined to be 447 mequiv (100 g)<sup>-1</sup>. It is close to the theoretical value [468 mequiv (100 g)<sup>-1</sup>], indicating that almost all of the Na<sup>+</sup> ions in the mica are exchangeable.

Fig. 5 shows the Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Ba<sup>2+</sup> uptake kinetics from a 0.5 M NaCl background solution with the Na-4-mica. The Cu<sup>2+</sup> and Pb<sup>2+</sup> were rapidly taken up, *i.e.* in less than 2 h. The order of the kinetic selectivity for these bivalent heavy metal ions was Cu > Pb > Ba > Zn > Cd. Fig. 6 shows the relationship between M<sup>2+</sup> exchanged with time as described by

**Table 2** Regression equations and coefficients of determination for M<sup>2+</sup> exchange using the modified Freundlich model

| Metal ion        | Regression equation  | r <sup>2</sup> |
|------------------|----------------------|----------------|
| Cu <sup>2+</sup> | -0.626 + 0.238 log t | 0.977          |
| Pb <sup>2+</sup> | -0.935 + 0.294 log t | 0.991          |
| Ba <sup>2+</sup> | -1.08 + 0.323 log t  | 0.978          |
| Zn <sup>2+</sup> | -1.59 + 0.385 log t  | 0.848          |
| Cd <sup>2+</sup> | -1.67 + 0.262 log t  | 0.843          |

the modified Freundlich model. For Cu<sup>2+</sup>, Pb<sup>2+</sup> and Ba<sup>2+</sup> exchange, the r<sup>2</sup> values ranged from 0.977 to 0.991 (Table 2) and thus describe the M<sup>2+</sup> exchange process well. However, the r<sup>2</sup> values were less than 0.85 for Zn<sup>2+</sup> and Cd<sup>2+</sup> exchange. For these two metal ions, the mechanism of the cation exchange kinetics may be different from that for Cu<sup>2+</sup>, Pb<sup>2+</sup> and Ba<sup>2+</sup>.

### Conclusions

With hydrated and well-dispersed Na-4-mica particles of about 2 μm in size, the order of the kinetic selectivity was determined to be Cu > Pb > Ba > Zn > Cd. The Cu and Pb uptake kinetics were especially very effective even with a very low metal concentration of less than 0.0001 M. This high level of decontamination of Cu and Pb is a very important separation which is required for purification of drinking water as well as for waste water treatment and disposal. The modified Freundlich model described the Cu, Pb and Ba ion exchange process as well.

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