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Interfering Effect for the Cesium Ion-Exchange Property of Sodium Difluorotetrasilicate and Sodium Taeniolite by Alkaline-Earth Metal Ions

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The cesium ion-exchange behavior of sodium difluorotetrasilicate (Na-TSM) and sodium taeniolite (Na-TAE) was investigated in the presence of alkaline-earth metal ions. When Na-TSM was exchanged beforehand with alkaline-earth metal ions, the amount of ion-exchanged Cs^+ decreased slightly compared to untreated Na-TSM. In contrast, when Cs^+-TSM was used very little ion exchange occurred with alkaline-earth metal ions. The interlayer spacing of Na-TSM contracted during the ion-exchange reaction with Cs^+ because interlayer water molecules were displaced. For the alkaline-earth metal ion exchange, interlayer water molecules were retained. Thus, the Cs^+ exchange occurred on Na-TSM that was exchanged beforehand with alkaline-earth metal ions. The Cs^+ exchange was superior to that observed for alkaline-earth metal ions in the mixed solutions. In contrast, the ion-exchange reaction occurred under all conditions examined with Na-TAE. In particular, even Cs^+ exchange was observed on Na-TAE that was exchanged beforehand with alkaline-earth metal ions. Furthermore, alkaline-earth metal ions exchange was observed on Cs^+-TAE.

Increased use of nuclear power generation has created a serious worldwide problem with the safe storage and disposal of nuclear waste. Japan plans to use stratigraphic procedures for the final disposal of nuclear waste, and related research is proceeding in sectors such as the design of suitable canisters and buffer materials.[1–4] Research on buffer materials is important because they represent the final barrier in the prevention of radioactive leakage. The synthetic sodium mica, sodium difluorotetrasilicate ($Na[Mg_{2.5}Si_4O_{10}F_2]\cdot 2H_2O$ or Na-TSM), has high ion-exchange selectivity for cesium ions, making it a promising buffer material.[5] We have reported on the comparison of Na-TSM to sodium taeniolite ($Na[LiMg_2Si_4O_{10}F_2]\cdot 2H_2O$ or Na-TAE) that is also a member of the mica family. Substituting Li for Mg in the Na-TSM skeleton greatly changes the swelling properties of the material because Na-TSM uptakes over ten water molecules vertically between lamellae. Indeed, Na-TSM is referred to as a "free-swelling clay mineral." By contrast, Na-TAE is known as a limited-swelling clay mineral because it intercalates only up to a maximum of two water molecules. Na-TAE absorbs more cesium ions than Na-TSM even though its ion-exchange selectivity among alkali metal ions is poor.[5] If Na-TAE is to be used as a buffer material, it is important that the material is unaffected by the presence of Sr and Ba in the nuclear waste. There is a paucity of research on the ion-exchange behavior of these buffer materials with cesium and alkaline-earth metal ions. A few reports have dealt with the ion-exchange behavior of Na-TAE for alkaline-earth metal ions with potassium ions,[6] and cesium ions.[7] In this paper, we focus on the interfering effect of alkaline-earth metal ions for cesium ion exchange on Na-TSM and Na-TAE.

Experimental

Materials. Ultra-purified water (UPW) with a specific resistance of 18.2 MΩ cm (Puric-R System, Japan Organo Co., Ltd.) was used in all experimental preparations unless stated otherwise. Na-TSM was purchased from Topy Industries Limited (Tokyo, Japan) and prepared as reported elsewhere.[5] Commercially available 10% Na-TSM sol was washed several times with UPW and the precipitated powder filtered and air-dried. Na-TAE provided by Topy Industries was used without pretreatment. Alkali and alkaline-earth metal ion solutions were prepared from chloride salts (Kanto Chemical Co., Inc., Tokyo, Japan).

Characterization. The exchanged samples were filtered and air-dried and subjected to characterization at once. A powder X-ray diffractometer (MO3X-HF, Mac Science Co., Ltd., Yokohama, Japan) equipped with monochromized Cu Kα radiation, $\lambda = 0.1541$ nm, was used to characterize Na-TSM before and after the ion-exchange reaction. Thermal analysis, thermogravimetry (TG) and differential thermal analysis (DTA) were conducted using a TG/DTA system (Thermoflex TAS 200 with Thermo Plus 2, Rigaku Corporation, Tokyo, Japan). Heating was at 10 °C min^{-1} and the sampling interval was 0.5 s.

Analysis. An atomic absorption spectrophotometer (AAS) (Hitachi Z-2300, Hitachi, Ltd., Tokyo, Japan) was used to determine the concentration of cesium ions. 2.0 g dm^{-3} of sodium chloride was added to each standard solution and sample solution to avoid experimental error caused by sodium ions from Na-TSM during the ion-exchange reaction. An inductively coupled plasma atomic emission spectrometer (ICP) (Shimadzu ICPS-5000, Shimadzu Corp. Kyoto, Japan) was used to determine the concentration of alkaline-earth metal ions.

Ion-Exchange Reaction. The distribution coefficient (K_d) values of the ion-exchange reaction with calcium, strontium, and ba-

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rium ions was determined as follows: 0.1 g of Na-TSM was immersed in 10 cm^3 of a solution containing 10, 5.0, 1.0, and 0.50 mM (M = mol dm^{-3}) of individual alkaline-earth metal ions at 60 °C for 48 h. To obtain the highest reaction rate under the open system, 60 °C was chosen as reaction temperature. The ion-exchangeability of Na-TAE for the alkali metal ions examined is ten-fold that of Na-TSM.[5] This result will be adapted into the ion-exchange reaction with alkaline-earth metal ions because ion exchange mainly occurs with interlayer cations. Therefore, the reactant solutions for Na-TAE were prepared at a concentration five times greater than those used for Na-TSM. Polypropylene containers were used to avoid adventitious contamination due to sodium ions from glass vessels. After equilibration, the supernatant solution was filtered through a 0.8 µm microdisk (Toyo Roshi Kaisha, Ltd., Tokyo, Japan) and the amount of metal ions remaining in the supernatant solution was determined by ICP. The amount of metal ions sorbed in the exchanger phase was estimated from the difference between the initial and final concentration in the supernatant solution. K_d was calculated as follows:

$$K_d = \frac{\text{Mole of metal ions in the exchanger phase}}{\text{Mole of metal ions in the solution phase}} \times \frac{\text{volume of the solution (cm}^3\text{)}}{\text{mass of the exchanger (g)}} \tag{1}$$

Two types of pre-treated Na-TSM and Na-TAE were used in the ion-exchange study. One was Cs^+-exchanged material, which was named Cs-TSM or Cs-TAE, whilst the other was exchanged with alkaline-earth metal ions, which was named M-TSM or M-TAE (M was alkaline-earth metal ion). These materials were used in place of Na-TSM or Na-TAE.

The coexistence of alkaline-earth metal ions in the cesium ion-exchange reaction was determined as follows: 0.1 g of Na-TSM was immersed in 10 cm^3 of mixture solutions, which consisted of 10 mM of cesium ions and 5.0 mM of individual alkaline-earth metal ions at 60 °C for 48 h. Five-fold greater concentration of reactants was used for Na-TAE. After equilibration, the metal ion concentration was measured as in the K_d study above, except that AAS was used for cesium ion determination.

Results and Discussion

Ion-Exchange Selectivity. The alkaline-earth metal ion-exchange properties of Na-TSM and Na-TAE were surveyed in order to compare with that of cesium ions. Figures 1a and 1b show the K_d values for alkaline-earth metal ions as a function of the concentration on Na-TSM and Na-TAE. The K_d curve of Mg^{2+} differs from the others in Figure 1a. In the cesium ion exchange on Na-TSM, the ion-exchange reaction occurred with lattice magnesium ions in addition to interlayer sodium ion stoichiometry.[5] Because this phenomenon is applicable to the ion-exchange reaction with alkaline-earth metal ions, the amount of magnesium ion sorbed onto Na-TSM could not be measured because the concentration of Mg^{2+} released from the lattice needed to be measured simultaneously. For this reason, magnesium ions were excluded from the remainder of this study. With the exception of magnesium ions, no great difference in the ion-exchange tendency was found between Na-TSM and Na-TAE as ion exchangers. Both materials had excellent exchangeability for calcium, strontium, and barium ions, especially at low concentrations, because the K_d values exceeded 1000 cm^3 g^{-1}. This trend is similar to cesium ion exchange.[5] No significant difference in the ion-exchange tendency was observed among the three alkaline-earth metal ions.

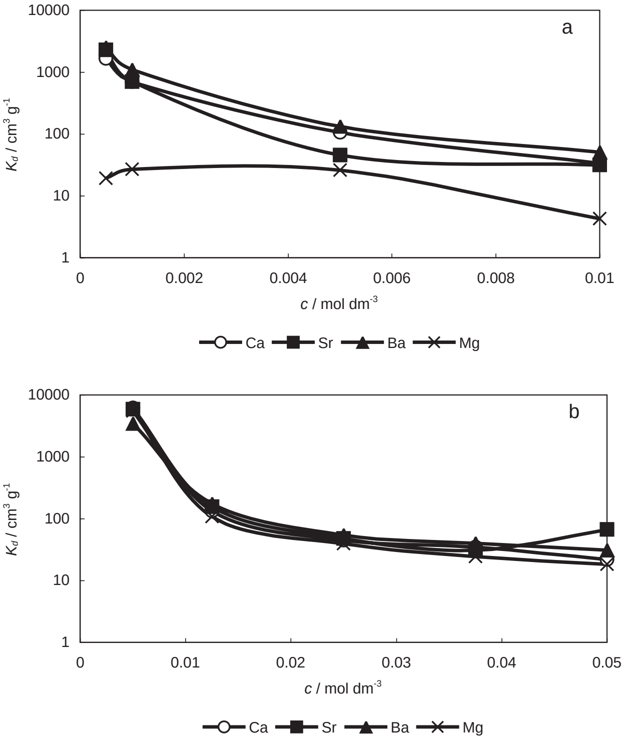

Figure 1. K_d values of alkaline-earth metal ions on Na-TSM (a) and Na-TAE (b). ○: Ca^{2+}, ■: Sr^{2+}, ▲: Ba^{2+}, ×: Mg^{2+}.

Table 1. Exchange Ratio of Ions Sorbed onto Na-TSM and Na-TAE[a)]

		Cs/%		M/%	
	M	isolated	mixed	isolated	mixed
Na-TSM	Ca	53.7	64.6	58.4	4.7
	Sr		53.4	49.3	3.6
	Ba		61.7	53.6	13.1
Na-TAE	Ca	70.8	99.7	57.6	61.6
	Sr		99.6	60.8	58.6
	Ba		99.4	63.2	67.6

a) Reactants: Initial concentrations: Cs^+ 1.0×10^{-2} mol dm^{-3}, M^{2+} 5.0×10^{-3} mol dm^{-3} (Na-TSM); Cs^+ 2.50×10^{-2} mol dm^{-3}, M^{2+} 1.25×10^{-2} mol dm^{-3} (Na-TAE). Volume: 10 cm^3. Weight of exchangers: 0.1 g.

Table 1 summarizes the ratio of the amount of sorbed ions in isolated ion solutions and mixed ion solutions. Because a K_d of 100 cm^3 g^{-1} indicates about 50% of the ion-exchange reaction, the initial concentration of reactants was prepared at this concentration. In mixed ion solutions such as (Ca^{2+} + Cs^+), (Sr^{2+} + Cs^+), and (Ba^{2+} + Cs^+), the exchange ratio of sorbed cesium ions became even higher compared to those of isolated solutions for both exchangers. However, the exchange ratio of sorbed alkaline-earth metal ions was dramatically reduced by the reaction with Na-TSM. A difference was not seen in the reaction with Na-TAE, presumably due to the competi-

Table 2. Exchange Ratio of Ions Sorbed onto the Different Exchangers[a)]

M	Ion-exchanged M^{2+} by Cs-TSM[b)]/%	Ion-exchanged Cs$^+$ by M-TSM[c)]/%
Ca	5.4	35.0
Sr	2.7	50.3
Ba	4.5	46.1

a) Reactants: Initial concentrations: Cs$^+$ 1.0×10^{-2} mol dm^{-3}, M^{2+} 5.0×10^{-3} mol dm^{-3}; Volume: 10 cm^3; Weight of exchangers: 0.1 g. b) Previously ion exchanged with Cs$^+$. c) Previously ion exchanged with M^{2+}.

Table 3. Exchange Ratio of Ions Sorbed onto the Different Exchangers[a)]

M	Ion-exchanged M^{2+} by Cs-TAE[b)]/%	Ion-exchanged Cs$^+$ by M-TAE[c)]/%
Ca	77.6	70.0
Sr	55.1	80.0
Ba	28.6	99.4

a) Reactants: Initial concentrations: Cs$^+$ 1.0×10^{-3} mol dm^{-3}, M^{2+} 5.0×10^{-4} mol dm^{-3}; Volume: 10 cm^3; Weight of exchangers: 0.1 g. b) Previously ion exchanged with Cs$^+$. c) Previously ion exchanged with M^{2+}.

tive reaction of ion-exchange sites between cesium ions and alkaline-earth metal ions on Na-TSM. Table 2 summarizes the exchange ratio of sorbed ions in different ion exchangers for Na-TSM. The center column in Table 2 shows the exchange ratio of ion-exchanged alkaline-earth metal ions using cesium ion-exchanged Na-TSM (Cs-TSM). The column on the right of Table 2 shows the exchange ratio of ion-exchanged cesium ions by Na-TSM that previously exchanged ions with alkaline-earth metal ions (M-TSM). Present results suggest that the mechanism of the ion-exchange reaction for cesium ions involves both the competition for ion-exchange sites with alkaline-earth metal ions and the extraction of exchanged ions. Very little exchange of alkaline-earth metal ions with cesium ions that were previously ion exchanged on Na-TSM was observed. The availability of interlayer sites for cation exchange generally depends on the degree of hydration of ions present in the interlayer region. Cations with low hydration energy, such as K$^+$, Rb$^+$, and Cs$^+$, shed their hydration shell in clay interlayers. Dehydration of these ions enables a close approach to tetrahedral silicate sheets and the formation of polar covalent bonds with structural oxygen atoms. Cesium ions bound to dehydrated interlayer sites are not readily exchanged by other cations and are usually considered "fixed."[8] The present results concur with this theory. Indeed, this phenomenon was subsequently supported by powder X-ray diffraction and thermal analysis as discussed later. A different tendency was obtained for pre-treated TAEs. Uptake of alkaline-earth metal ions onto Cs-TAE and cesium ion onto M-TAE were similar except for Ba^{2+} as shown in Table 3. Further examination is necessary, however, to clarify this phenomenon.

Powder X-ray Diffraction Analysis. Figure 2 shows powder X-ray diffraction patterns of (a) Na-TSM and (b) Na-TAE before and after ion exchange with alkaline-earth metal ions. The pattern of cesium ion exchange is shown for comparison. Na-TSM has an interlayer spacing of 1.5 nm with two water molecules assigned to the strong peak at the far left of Figure 2a. This peak shifts to the right after ion exchange with cesium ions and the interlayer spacing is about 1.0 nm. Thus, the ion-exchange reaction must proceed by the withdrawal of water molecules from the Na-TSM interlayer. For alkaline-earth metal ions, interlayer spacing remains unchanged at 1.5 nm (Figure 2a), indicating that the water molecules between the layers are retained after the ion-exchange reaction. However, following the ion-exchange reaction with Cs$^+$ on Na-TAE, the layer structure is disrupted as water molecules are extracted. With alkaline-earth metal ions, the interlayer distance was maintained, or possibly even extended. These results may explain why the ion-exchange distribution arose for mixed reactants (Table 1).

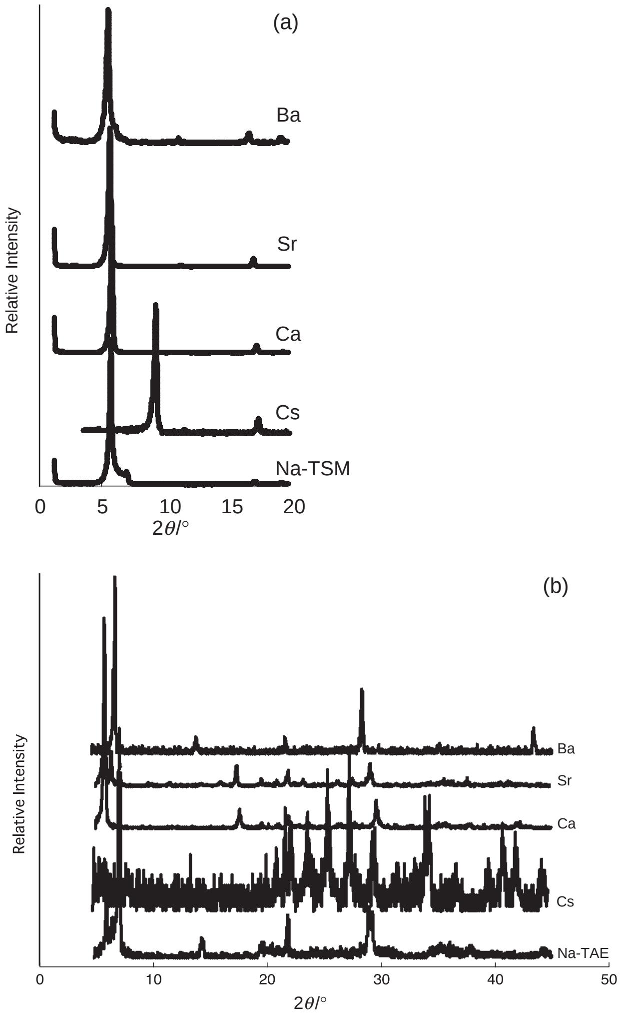

Figure 2. Powder X-ray diffraction patterns of Na-TSM (a) and Na-TAE (b) before and after the ion-exchange reaction with alkaline-earth metal ions and cesium ion.

Figure 3 shows powder X-ray diffraction patterns for (a) Na-TSM and (b) Na-TAE after ion-exchange with the mixed solution of cesium and alkaline-earth metal ions. Strong diffraction peaks are observed as for the isolated cesium ion-exchange sample with a split side peak as seen in Figure 3a.

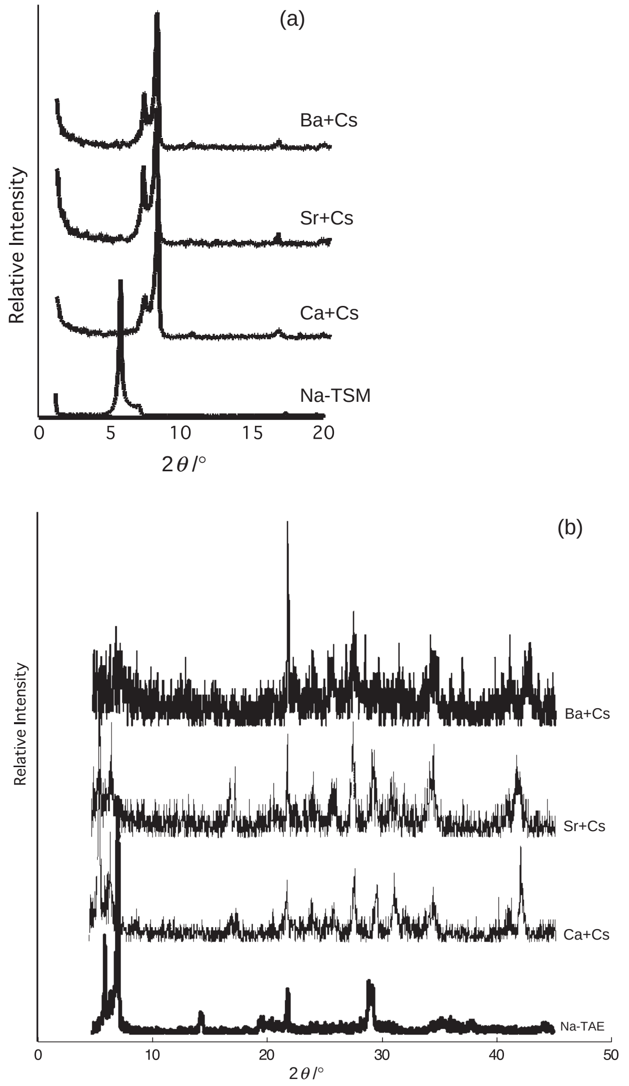

Figure 3. Powder X-ray diffraction patterns Na-TSM (a) and Na-TAE (b) before and after ion exchange with mixed reactants.

The interlayer spacing of Na-TSM clearly shrank during the ion-exchange reaction when cesium ions were present in the reactant. In this case, very little coexistent alkaline-earth metal ions sorbed to Na-TSM, showing that the water molecules between the layers are required in order to maintain the interlayer spacing for alkaline-earth metal ion exchange. By contrast, the large interlayer distance of Na-TAE, which is maintained by water molecules, facilitates the uptake of alkaline-earth metal ions from mixed reactant solutions (Table 1) after the ion-exchange reaction (Figure 3b). The diffraction pattern for $Ba^{2+} + Cs^{+}$ reactant differs slightly from other mixed reactants. Ba^{2+} displays unique ion-exchange behavior on Na-TAE. More investigation is required to clarify this phenomenon. This phenomenon is also observed when alkaline-earth metal ions exist as contaminants.

Figure 4 shows DTA curves for (A) Na-TSM and (B) Na-TAE before and after the ion-exchange reaction with Cs^{+}, Sr^{2+}, and their mixed solutions. Data on other reactants were similar to those described here and have therefore been omitted.

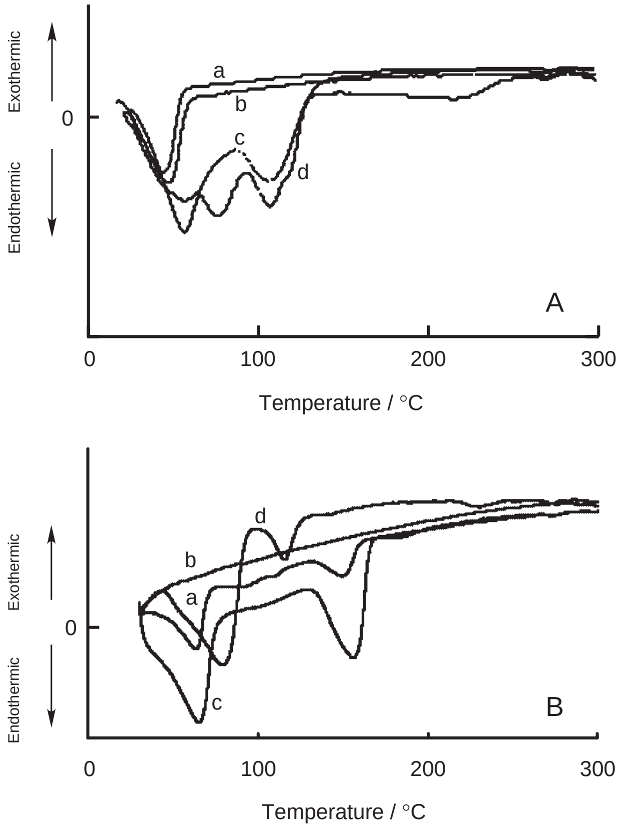

Figure 4. DTA curves of Na-TSM (A) and Na-TAE (B) after ion exchange with ($Cs^{+} + Sr^{2+}$) (a), Cs^{+} (b), Sr^{2+} (c), and unreacted materials (d).

Only one endothermic peak is seen after the reaction with (a) the mixed solution and (b) the Cs^{+} solution on Na-TSM (Figure 4A), inferring that water molecules were lost from the interlayer during the reaction. Two peaks are seen in the reaction with Sr^{2+} (c), showing some water molecules are retained between layers. In contrast to Na-TSM, the reaction with mixed solutions on Na-TAE (Figure 4B-a) display two peaks, as shown in Figure 4B-c. Alkaline-earth metal ions thus serve to maintain water molecules between layers, which is why the cesium ion exchange occurred in the mixed reactant and with M-exchanged TAE. These observations agree with studies on ion-exchange selectivity and powder X-ray diffraction.

Conclusion

The ion-exchange behavior of alkaline-earth metal ions on Na-TSM and Na-TAE was similar for the reaction with isolated ion solutions but differed dramatically in the presence of cesium ions. However, the ratio of ion exchanged alkaline-earth metal ions decreased dramatically when Cs-TSM was used. Furthermore, except for Ba^{2+}, Cs-TAE exchanged with alkaline-earth metal ions to almost the same extent as Na-TAE. In terms of the cesium ion-exchange reaction, both materials showed excellent exchange ability. Na-TSM is a particularly suitable material when Cs^{+} collects separately from the alkaline-earth metal ions. However, Na-TAE is superior to Na-TSM as a buffer material for stratum disposal because it uptakes both Cs^{+} and Sr^{2+}. This is an important property because radioactive strontium is generated from nuclear disintegration of waste material. In addition, Na-TAE shows higher exchange ability for Cs$^+$ compared to Na-TSM.

References

1 O. L. Cherif, H. Sakashita, T. Kumada, *Nihon Genshiryoku Gakkaishi* **2001**, *43*, 924.

2 K. Iriya, N. Takeda, S. Sogo, *Obayashigumi Gijutsu Kenkyushoho* **2003**, *66*, 63.

3 T. Tsushima, M. Suzuki, N. Akao, N. Hara, K. Sugimoto, *Zairyo-to-Kankyo* **2003**, *52*, 92.

4 Y. Onodera, *Nendo Kagaku* **2003**, *42*, 132.

5 N. Suzuki, D. Yamamoto, N. Anaguchi, H. Tsuchiya, K. Aoki, Y. Kanzaki, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2599.

6 M. Miyake, T. Suzuki, T. Suzuki, *Chem. Mater.* **1993**, *5*, 1327.

7 T. Suzuki, S. Sakata, T. Hatsushika, S. Sugita, H. Sakane, *Bull. Soc. Sea Water Sci., Jpn.* **1994**, *48*, 427.

8 R. N. J. Comans, M. Haller, P. De Preter, *Geochim. Cosmochim. Acta* **1991**, *55*, 433.