



# Cs<sup>+</sup> and Sr<sup>2+</sup> adsorption selectivity of zeolites in relation to radioactive decontamination

M.W. Munthali<sup>a,\*</sup>, E. Johan<sup>b</sup>, H. Aono<sup>b</sup>, N. Matsue<sup>a</sup><sup>a</sup> Department of Life Environmental Conservation, Faculty of Agriculture, Ehime University, 3-5-7 Tarumi, Matsuyama 790-8566, Japan<sup>b</sup> Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan

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## ABSTRACT

Zeolites are used as adsorbents of cationic elements in the radioactive decontamination process of water, soil and others. We determined Cs<sup>+</sup> and Sr<sup>2+</sup> adsorption selectivity of some zeolites to know effective zeolite species for the decontamination of radioactive Cs and Sr. A 30 mL mixed solution containing up to 15 mg L<sup>-1</sup> of non-radioactive Cs<sup>+</sup> or Sr<sup>2+</sup> and up to 0.50 M of Na<sup>+</sup> or K<sup>+</sup> was mixed with 0.5 g of Linde-type A, Na-P1, faujasite X, faujasite Y and mordenite. Among the zeolites, mordenite had the highest Cs<sup>+</sup> adsorption selectivity, and the selectivity had no correlation to the cation exchange capacity (CEC) of the zeolites. In contrast, Sr<sup>2+</sup> adsorption selectivity of the zeolites positively correlated with the CEC of the zeolites; Linde-type A with the highest CEC showed the highest adsorption selectivity, and its adsorption rate was more than 99.9% even in the presence of 0.5 M K<sup>+</sup>. A simulated soil decontamination experiment of Cs from a Cs-retaining vermiculite by using mordenite and that of Sr from a Sr-retaining vermiculite by using Linde-type A showed decontamination rates of more than 90%.

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## 1. Introduction

Over the past years, many anthropogenic activities have generated unacceptable levels of radioactive materials such as <sup>137</sup>Cs (strong beta–gamma emitter) and <sup>90</sup>Sr (beta emitter) with half-life of about 30 years [1–3]. Their high potential of accumulation in plants and animals causes serious environmental and human health problems such as carcinogenic diseases like leukemia and skin cancer [4–6]. The radioactive elements are released into the environment through the discharge of nuclear waste effluents, nuclear weapon testing and nuclear power accidents such as in Fukushima, which contaminated forest, soil, water body, and so on [7–9]. In soil, immobilized radionuclides are further released to groundwater due to acidification, dissolution of solid phase, competitive adsorption with other cations, and complexation by ligands [10]. The contamination by the radioactive Cs and Sr is likely to continue raising many environmental concerns on the safety of agricultural soil, drinking water, irrigation water and crops [4,11].

Currently, the removal of radioactive Cs and Sr from the environment involves precipitation, adsorption by cation exchange, vacuum evaporation, reverse osmosis, filtration and solvent extraction, phytoextraction, electrodialysis, and so on [12–14]. Among the methods, adsorptive removal by zeolites is attractive and promising due to its simplicity, specific cation selectivity, high efficiency, low cost, superior chemical stability and thermal resistance [1,14–17]. Zeolites have been widely used in agriculture, nuclear industry, detergent industry, and environmental protection as selective cation exchangers [18–21]. In the decontamination of radioactive Cs and Sr, many adsorption experiments used natural zeolites such as mordenite and clinoptilolite, and synthetic zeolites such as Linde-type A, faujasite X and a blend of them [22–27].

The amount of released radioactive Cs and Sr in the environment varies widely ranging from 0 to 5 mg per 1 L of aqueous solution or per 1 kg of soil [3,9,28,29]. In the environment, various species of cations exist including non-radioactive Cs and Sr, and their total amount is much greater than the targeted radioactive Cs<sup>+</sup> and Sr<sup>2+</sup> [30,31]. The various coexistence cations interfere with the adsorption of the radioactive Cs<sup>+</sup> and Sr<sup>2+</sup> by zeolites during the decontamination process. The adsorption of the radioactive cations by zeolites is also influenced by the CEC and framework structure of zeolites, and by the chemical species and concentration of solutes in aqueous phase [32–34]. However, little research

\* Corresponding author. Tel.: +81 89 946 9681; fax: +81 89 977 4364.

E-mail address: [munthaliw@yahoo.co.uk](mailto:munthaliw@yahoo.co.uk) (M.W. Munthali).

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work compared the adsorption selectivity of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  by various zeolites under different electrolyte concentrations and types of coexistence cations. In this study, we evaluated the adsorption selectivity of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  by some zeolites under different concentrations of  $\text{Na}^+$  or  $\text{K}^+$  as a coexistence cation. Then, we proposed efficient zeolite species to be used for each decontamination of radioactive  $\text{Cs}^+$  and  $\text{Sr}^{2+}$ , and a few simulated decontamination experiments of artificially Cs- and Sr-adsorbed vermiculites were carried out by using each efficient zeolite species.

## 2. Materials and methods

All chemical reagents and synthetic zeolites (Linde-type A, faujasite X, faujasite Y and mordenite) used in this study were obtained from Wako Chemicals Ltd., Japan. The reagents of Cs and Sr were non-radioactive ones. Na-P1 zeolite was hydrothermally synthesized from chemical reagents [35]. The CEC values of the zeolite samples are  $5.56 \text{ mmol g}^{-1}$  in Linde-type A,  $4.40 \text{ mmol g}^{-1}$  in faujasite X,  $4.29 \text{ mmol g}^{-1}$  in Na-P1,  $2.40 \text{ mmol g}^{-1}$  in faujasite Y, and  $1.76 \text{ mmol g}^{-1}$  in mordenite [36].

We prepared  $\text{Na}^+$ -saturated samples of Linde-type A, Na-P1, faujasite X, faujasite Y and mordenite by washing the zeolites with a 1 M  $\text{NaNO}_3$  solution, followed by washing with water. Each 0.5 g of the  $\text{Na}^+$ -saturated zeolite was put into a 50 mL centrifuge bottle, and 30 mL of nitrate solution containing 0–15  $\text{mg L}^{-1}$   $\text{Cs}^+$  or  $\text{Sr}^{2+}$  ( $\text{Cs}^+$ : 0–113  $\mu\text{M}$ ,  $\text{Sr}^{2+}$ : 0–171  $\mu\text{M}$ ) was added. In the solution,

0.05, 0.10 or 0.50 M of  $\text{NaNO}_3$  or  $\text{KNO}_3$  coexisted. We must note here that the amount of positive charge of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  added was less than 1.2% of the negative charge of the zeolites. The bottle was shaken in a water bath for 1 h at a constant temperature of  $25 \pm 0.2^\circ\text{C}$ , and centrifuged at  $2000 \times g$  for 10 min. The reaction time of 1 h was determined in the preliminary experiments. The concentrations of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  in the supernatant were measured by an atomic absorption spectrophotometer (AAS: Hitachi Z-5000), and the amounts of adsorption of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  were calculated from the difference between their initial and final concentrations. Another experiment was set up similar to above with a fixed initial  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  concentration of  $10 \text{ mg L}^{-1}$  under the same temperature of  $25^\circ\text{C}$ . The data from this experiment was used to calculate a distribution coefficient ( $K_d$ ) [39] and adsorption ratio. The distribution coefficient ( $K_d$ ) was calculated by the following equation:

$$K_d (\text{mL g}^{-1}) = [(A_i - A_f)/A_f] \times V/M \quad (1)$$

where  $A_i$  is initial concentration of  $\text{Cs}^+$  or  $\text{Sr}^{2+}$  ( $\text{mol L}^{-1}$ ),  $A_f$  is equilibrium concentration of  $\text{Cs}^+$  or  $\text{Sr}^{2+}$  ( $\text{mol L}^{-1}$ ),  $V$  is volume of solution phase (mL) and  $M$  is mass of the adsorbent (g) [37].

Simulated decontamination experiments of Cs- and Sr-contaminated soils were carried out by using a vermiculite sample ( $>150 \mu\text{m}$ ). The CEC of the vermiculite sample was measured by the method of Barshad and Kishk [38]. The vermiculite sample was washed with water, air-dried, and  $\text{CsNO}_3$  or  $\text{Sr}(\text{NO}_3)_2$  solution

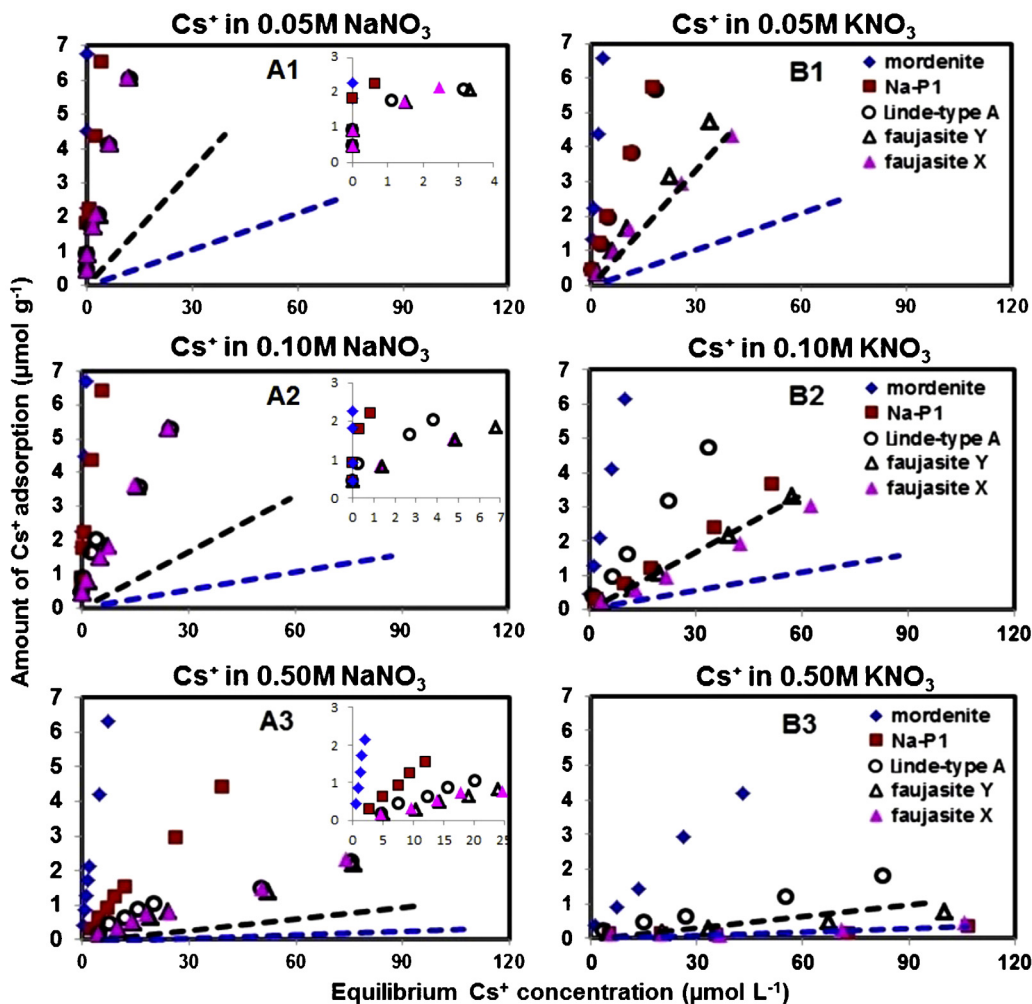


Fig. 1. Adsorption isotherms of  $\text{Cs}^+$  by zeolites. A1: in 0.05 M  $\text{NaNO}_3$ ; A2: in 0.10 M  $\text{NaNO}_3$ ; A3: in 0.50 M  $\text{NaNO}_3$ ; B1: in 0.05 M  $\text{KNO}_3$ ; B2: in 0.10 M  $\text{KNO}_3$ ; B3: in 0.50 M  $\text{KNO}_3$ .

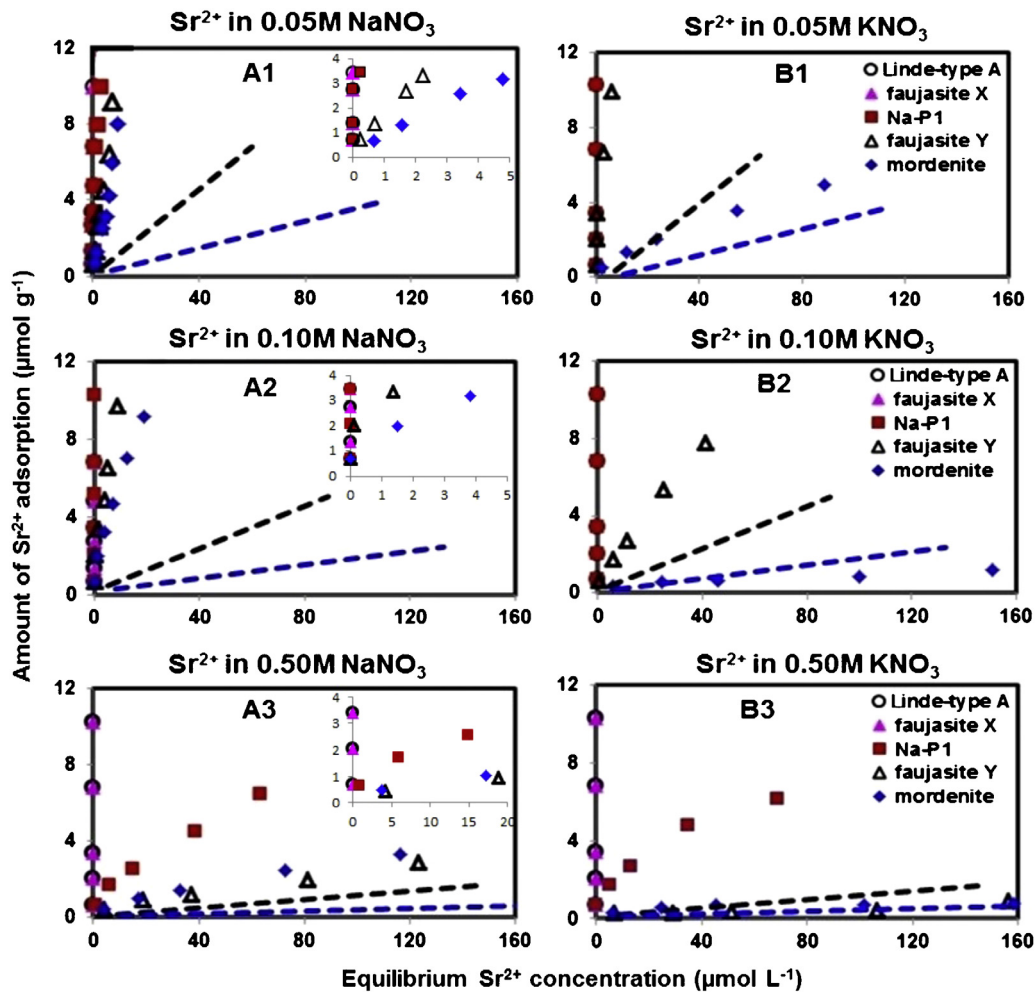


Fig. 2. Adsorption isotherms of  $\text{Sr}^{2+}$  by zeolites. A1: in 0.05 M  $\text{NaNO}_3$ ; A2: in 0.10 M  $\text{NaNO}_3$ ; A3: in 0.50 M  $\text{NaNO}_3$ ; B1: in 0.05 M  $\text{KNO}_3$ ; B2: in 0.10 M  $\text{KNO}_3$ ; B3: in 0.50 M  $\text{KNO}_3$ .

was added to obtain Cs- or Sr-retaining vermiculite; the amount of retention of Cs and Sr was set to  $60 \text{ mg kg}^{-1}$ . The Cs- and Sr-retaining vermiculites were washed with water, air-dried, and used as simulated Cs- and Sr-contaminated soils. Then 2 g of the Cs-retaining vermiculite was mixed with 2 g of  $\text{Na}^+$ -saturated mordenite ( $<90 \mu\text{m}$ ) in a 250 mL polyethylene bottle, and 60 mL of 0.3 M KCl solution was added. The contents were shaken for 3 h, and vermiculite and mordenite were separated from each other by wet sieving using a  $105\text{-}\mu\text{m}$  sieve. The same experiment was also carried out by using the Sr-retaining vermiculite and  $\text{Na}^+$ -saturated Linde-type A ( $<90 \mu\text{m}$ ). Blank runs without the zeolites were also conducted. The contents of Cs of Cs-retaining vermiculite and Sr of Sr-retaining vermiculites before and after the decontamination experiment were determined by dissolving 1 g of the vermiculites with 30 mL of 3 M  $\text{HNO}_3$  at  $100^\circ\text{C}$  for 3 h and subsequent determination of Cs and Sr by AAS.

### 3. Results and discussion

#### 3.1. Analysis of adsorption isotherms

The equilibrium concentration of  $\text{Cs}^+$  and the amount of adsorption of  $\text{Cs}^+$  in the adsorption experiments gave  $\text{Cs}^+$  adsorption isotherms onto zeolites. Fig. 1 shows  $\text{Cs}^+$  adsorption isotherms onto  $\text{Na}^+$ -saturated Linde-type A, Na-P1, faujasite X, faujasite Y and mordenite zeolites in the presence of  $\text{NaNO}_3$  (A1: 0.05 M, A2: 0.1 M,

A3: 0.5 M) and  $\text{KNO}_3$  (B1: 0.05 M, B2: 0.1 M, B3: 0.5 M). In general, the  $\text{Cs}^+$  adsorption isotherms differed largely among the five zeolite species, and the amount of  $\text{Cs}^+$  adsorption decreased with increasing concentration of the coexistence cation. The species of coexistence cation also influenced the isotherm, and the coexistence of  $\text{K}^+$  decreased the amount of  $\text{Cs}^+$  adsorption much more than the coexistence of  $\text{Na}^+$  did.

In order to help further analysis of the isotherms, we calculated hypothetical stochastic adsorption isotherms by assuming that all of the cations contained in the present system,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$ , had the same adsorption selectivity onto the zeolites. In this study, 1 g of zeolite (0.88–2.78 mmol of framework negative charge), its exchangeable  $\text{Na}^+$  (0.88–2.78 mmol),  $\text{Cs}^+$  (0–0.0033 mmol), and  $\text{Na}^+$  or  $\text{K}^+$  as nitrate (1.5, 3, or 15 mmol) coexisted in a bottle. Therefore, division of the amount of zeolite negative charges by the total amount of cation charges gives a stochastic adsorption rate of  $\text{Cs}^+$ . The stochastic adsorption rate increases with increasing CEC value of the zeolite, and decreases with increasing concentration of the coexistence cation ( $\text{Na}^+$  or  $\text{K}^+$ ). When the concentration of added  $\text{NaNO}_3$  or  $\text{KNO}_3$  was 0.05 M, the stochastic adsorption rates were between 37.0% (mordenite) and 65.0% (Linde-type A). Similarly, the rates were between 22.7% and 48.1% with 0.10 M  $\text{NaNO}_3$  or  $\text{KNO}_3$ , and between 5.5% and 15.6% with 0.50 M  $\text{NaNO}_3$  or  $\text{KNO}_3$ . By using the calculated stochastic adsorption rates of mordenite and Linde-type A, we obtained their stochastic adsorption isotherms, and added them in Fig. 1 as dotted lines. Upper black

dotted lines are stochastic adsorption isotherms of Linde-type A, lower blue dotted lines are stochastic adsorption isotherms of mordenite, and stochastic adsorption isotherms of the other three zeolites are located between the two dotted lines (not shown).

The Cs<sup>+</sup> adsorption isotherms in Fig. 1 showed that mordenite had the highest Cs<sup>+</sup> adsorption among the zeolites under all conditions, although the CEC value of mordenite was the lowest among the five zeolites, as described earlier. The amount of Cs<sup>+</sup> adsorption onto mordenite was always far greater than the stochastic value, and the isotherms of mordenite were located far above the stochastic adsorption isotherms. In contrast, faujasite X with the second highest CEC showed the lowest adsorption in most cases; in the presence of 0.50 M KNO<sub>3</sub>, the adsorption isotherm of faujasite X was located under the stochastic adsorption isotherm of mordenite. Linde-type A with the highest CEC also showed much lower Cs<sup>+</sup> adsorption than mordenite did in all cases.

Fig. 2 shows Sr<sup>2+</sup> adsorption isotherms onto Na<sup>+</sup>-saturated Linde-type A, Na-P1, faujasite X, faujasite Y and mordenite zeolites in the presence of NaNO<sub>3</sub> (A1: 0.05 M, A2: 0.1 M, A3: 0.5 M) and KNO<sub>3</sub> (B1: 0.05 M, B2: 0.1 M, B3: 0.5 M). The same stochastic adsorption isotherms of Linde-type A and mordenite as Fig. 1 are also given. Similar to the adsorption of Cs<sup>+</sup>, in general, the Sr<sup>2+</sup> adsorption isotherms differed largely among the five zeolite species, and the amount of Sr<sup>2+</sup> adsorption decreased with increasing concentration of the coexistence cation. The coexistence of K<sup>+</sup> decreased the amount of Sr<sup>2+</sup> adsorption more than the coexistence of Na<sup>+</sup> did. The most remarkable feature of the adsorption isotherms of Sr<sup>2+</sup> was extremely high adsorption selectivity by Linde-type A and faujasite X. Even at the highest addition of Sr<sup>2+</sup> (15 mg L<sup>-1</sup>) in the presence of 0.50 M KNO<sub>3</sub>, the equilibrium concentration of Sr<sup>2+</sup> was lower than the detection limit of 0.01 mg L<sup>-1</sup>, and more than 99.9% of Sr<sup>2+</sup> was adsorbed by Linde-type A and faujasite X. This indicated that Linde-type A and faujasite X zeolites had very strong Sr<sup>2+</sup> adsorption sites in their structure. The amount of adsorption of Sr<sup>2+</sup> was the lowest in mordenite at most NaNO<sub>3</sub> and KNO<sub>3</sub> concentrations, and the Sr<sup>2+</sup> adsorption isotherms of mordenite in the presence of 0.1 and 0.5 M KNO<sub>3</sub> were located below the stochastic adsorption isotherm of mordenite.

### 3.2. Distribution coefficient and adsorption rate

From a viewpoint of the practical radioactive decontamination of water and soil using adsorbents, the distribution coefficient,  $K_d$ , that describes the distribution of an adsorbate between the surface of the adsorbent and aqueous phase is important. The values of  $K_d$  (mL g<sup>-1</sup>) for the adsorption of Cs<sup>+</sup> and Sr<sup>2+</sup> onto the zeolites are given in Table 1 with the values of adsorption rates of Cs<sup>+</sup> and Sr<sup>2+</sup>.

The  $K_d$  value of Cs<sup>+</sup> adsorption was the highest for mordenite among the five zeolites; the  $K_d$  value of mordenite was more than 1000 with 0.05 M NaNO<sub>3</sub>, 0.1 M NaNO<sub>3</sub> and 0.05 M KNO<sub>3</sub> addition, and the adsorption rate of Cs<sup>+</sup> exceeded 90% except when 0.5 M KNO<sub>3</sub> was added. With the addition of 0.05 M NaCl, the adsorption rate was more than 99.9% and the  $K_d$  value was more than 74,940 (detection limit was 0.008 mg-Cs L<sup>-1</sup>). The  $K_d$  of Sr<sup>2+</sup> adsorption was the highest for Linde-type A. In all cases, equilibrium Sr<sup>2+</sup> concentration with Linde-type A was less than the detection limit of 0.01 mg-Sr L<sup>-1</sup>, and all of the  $K_d$  values of Linde-type A were calculated as greater than 59,940, which is the  $K_d$  value when equilibrium Sr<sup>2+</sup> concentration was 0.01 mg L<sup>-1</sup>. Faujasite X also had high  $K_d$  values comparable to Linde-type A, but the  $K_d$  values of faujasite X were somewhat lower than 59,940 with 0.1 M and 0.5 M NaCl addition.

The  $K_d$  values in Table 1 suggested the Cs<sup>+</sup> and Sr<sup>2+</sup> adsorption selectivity sequences by the five zeolites as follows.

Cs<sup>+</sup> adsorption:

In the presence of NaNO<sub>3</sub>: mordenite > Na-P1 > Linde-type A ≈ faujasite X ≈ faujasite Y

In the presence of KNO<sub>3</sub>: mordenite > Linde-type A > Na-P1 > faujasite Y > faujasite X

Sr<sup>2+</sup> adsorption:

In the presence of NaNO<sub>3</sub>: Linde-type A ≈ faujasite X > Na-P1 > faujasite Y ≈ mordenite

In the presence of KNO<sub>3</sub>: Linde-type A > faujasite X > Na-P1 > faujasite Y > mordenite

The adsorption selectivity sequences of Cs<sup>+</sup> had no correlation to the CEC values of the zeolites, but the sequences of Sr<sup>2+</sup> had positive correlation to the CEC values of the zeolites.

The values of  $K_d$  for some synthetic adsorbents have been reported. The adsorbents with greater  $K_d$  values for the adsorption of Cs<sup>+</sup> are Prussian blue with a  $K_d$  value of 250,000 mL g<sup>-1</sup> and copper(II) ferrocyanide immobilized on mesoporous silica with  $K_d$  of greater than 1,400,000 mL g<sup>-1</sup>, both in the presence of 4500 ppm Na, 1000 ppm Mg, 200 ppm Ca, 100 ppm K, 1 ppm Se, and 0.5 ppm (each) of Mn, Fe, Co, Cu, Zn, and Mo [39]. The  $K_d$  values of mordenite against Cs<sup>+</sup> obtained in this study were lower than those of these synthetic adsorbents. However in most cases, the adsorption rate of Cs<sup>+</sup> onto mordenite exceeded 90% as described earlier, and natural mordenite-type zeolite samples are available with low price. The adsorbents for Sr<sup>2+</sup> with greater  $K_d$  values are sodium titanate with  $K_d$  of 235,120 mL g<sup>-1</sup> in the presence of 5 M Na<sup>+</sup> [40], and hydrous antimony pentoxide with  $K_d$  of 4,200,000 mL g<sup>-1</sup> in the presence of 0.1 M HNO<sub>3</sub> [41]. In this study, the  $K_d$  values of Linde-type A were greater than 59,940 mL g<sup>-1</sup>, but the adsorption rate of Sr<sup>2+</sup> exceeded 99.9% in all cases.

From these results, we concluded that zeolite species suitable for the decontamination of radioactive Cs<sup>+</sup> from water and soil is mordenite, although high concentration of coexistence K<sup>+</sup> may affect the decontamination efficiency. For the decontamination of radioactive Sr<sup>2+</sup> from water and soil, Linde-type A is suitable even in the presence of 0.5 M Na<sup>+</sup> and K<sup>+</sup>, and the use of Linde-type A is effective in the removal of Sr<sup>2+</sup> from sea water containing about 0.5 M of Na<sup>+</sup> and other cations.

The strong adsorption selectivity of mordenite for Cs<sup>+</sup> and Linde-type A for Sr<sup>2+</sup> can be explained by looking at the differences in their ionic diameters, the CEC values of the zeolites [36], and apertures (pore opening size) of the zeolites (Linde-type A: 11.4 Å, 6.6 Å, 4.1 Å and 2.2 Å; mordenite: 7.0 Å, 4.2 Å and 3.6 Å [20,35,42,43]). The adsorption selectivity of Sr<sup>2+</sup> by the zeolites had positive correlation to the CEC. For instance, the amounts of Sr<sup>2+</sup> adsorption were 99.9% and 4% for faujasite X (CEC: 4.40 mmol g<sup>-1</sup>) and faujasite Y (CEC: 2.40 mmol g<sup>-1</sup>), respectively, irrespective of having almost the same framework structure. This means the strong adsorption selectivity of Sr<sup>2+</sup> by Linde-type A is mainly due to strong electrostatic attraction forces related to the amount of negative charge density or CEC. In other words, in zeolites with high CEC such as Linde-type A, there are more attraction forces due to more available charge sites per unit cell which are close to each other than in zeolites with low CEC such as mordenite [44]. Considering the small size of Sr<sup>2+</sup> (i.e. Sr<sup>2+</sup> could penetrate in most of the pores of all zeolites) it means more Sr<sup>2+</sup> was more strongly attracted in Linde-type A than mordenite. This means the amount of electrostatic attractions affected the amount of Sr<sup>2+</sup> adsorption and selectivity level among the zeolites due to their differences in the separation distances of the framework charge sites [45]. This is why the Sr<sup>2+</sup> adsorption selectivity correlated well with amount of CEC of zeolites. However, the adsorption selectivity of Cs<sup>+</sup> had

**Table 1**

Distribution coefficient and adsorption ratio of Cs<sup>+</sup> and Sr<sup>2+</sup> by zeolites based on the initial fixed Cs<sup>+</sup> and Sr<sup>2+</sup> concentration of 10 mg L<sup>-1</sup>. The CEC value of each zeolite is given in parenthesis.

Cations added (M)			Linde-type A (5.56 mmol g <sup>-1</sup> )		Na-P1 (4.29 mmol g <sup>-1</sup> )		Faujasite X (4.40 mmol g <sup>-1</sup> )		Faujasite Y (2.40 mmol g <sup>-1</sup> )		Mordenite (1.76 mmol g <sup>-1</sup> )	
			K <sub>d</sub> (mL g <sup>-1</sup> )	Ads. ratio (%)	K <sub>d</sub> (mL g <sup>-1</sup> )	Ads. ratio (%)	K <sub>d</sub> (mL g <sup>-1</sup> )	Ads. ratio (%)	K <sub>d</sub> (mL g <sup>-1</sup> )	Ads. ratio (%)	K <sub>d</sub> (mL g <sup>-1</sup> )	Ads. ratio (%)
Cs <sup>+</sup>	Na <sup>+</sup>	0.05	645	91.4	1796	96.8	657	91.6	663	91.7	>74,940	>99.9
		0.10	223	78.8	1676	96.5	252	80.8	237	79.8	6013	99.0
		0.50	30	33.1	111	64.8	30	33.1	27	30.9	833	93.2
	K <sup>+</sup>	0.05	320	84.2	340	84.9	116	65.9	141	70.1	2094	97.0
		0.10	141	70.1	67	52.9	46	43.2	55	47.9	636	91.4
		0.50	22	26.7	2	3.3	4	5.7	7	10.9	112	65.0
Sr <sup>2+</sup>	Na <sup>+</sup>	0.05	>59,940	>99.9	15,404	99.6	>59,940	>99.9	3581	98.4	2000	97.1
		0.10	>59,940	>99.9	13,893	99.5	52,114	99.9	893	93.9	410	89.2
		0.50	>59,940	>99.9	254	80.8	45,395	99.8	78	56.4	76	55.9
	K <sup>+</sup>	0.05	>59,940	>99.9	>59,940	>99.9	>59,940	>99.9	2254	97.4	65	51.9
		0.10	>59,940	>99.9	>59,940	>99.9	>59,940	>99.9	210	77.8	9	12.4
		0.50	>59,940	>99.9	136	69.4	>59,940	>99.9	4	6.6	7	10.8

no correlation to the CEC values of the zeolites, and mordenite with the lowest CEC showed the highest Cs<sup>+</sup> adsorption selectivity while for faujasite X and faujasite Y (with different CEC but same structural framework) it was quite similar (Fig. 1 and Table 1). This means the strong adsorption selectivity of Cs<sup>+</sup> by mordenite was due to the differences in apertures (i.e. mordenite smaller than Linde-type A), and hydration energy and hydration number of Cs<sup>+</sup> (diameter of 3.34 Å) being smaller than those of Sr<sup>2+</sup> (2.26 Å), Na<sup>+</sup> (2.02 Å) and K<sup>+</sup> (2.76 Å) [43,46–51]. It is possible that dehydrated or partially hydrated Cs<sup>+</sup> is strongly fixed at 3.6 Å aperture of mordenite, but further study is needed to confirm this.

### 3.3. Simulated soil decontamination

In the preparation of Cs- and Sr-retaining vermiculites (60 mg kg<sup>-1</sup>), almost all the added Cs<sup>+</sup> and Sr<sup>2+</sup> were adsorbed onto the vermiculite. This was so because CEC of the vermiculite was 125 cmol kg<sup>-1</sup>, and the ratio of the positive charge of the cations included in the system to the negative charge of vermiculite was nearly unity (<1.001). The retained Cs<sup>+</sup> and Sr<sup>2+</sup> hardly desorbed by the washing with 0.3 M KCl as shown in Fig. 3; 98.5% of Cs and 93.0% of Sr remained in vermiculite. Since 2 g of vermiculite with CEC of 125 cmol kg<sup>-1</sup> was washed with 60 mL of 0.3 M KCl, a stochastic rate of Cs<sup>+</sup> and Sr<sup>2+</sup> that remained in vermiculite is calculated as 12.2%, much lower than the observed remaining rates shown above. These indicated that Cs<sup>+</sup> and Sr<sup>2+</sup> in the Cs- and Sr-retaining vermiculites were very strongly held by the vermiculite, and hardly desorbed by the washing with 0.3 M KCl. In contrast, when mordenite or Linde-type A coexisted with vermiculite and 0.3 M KCl, the remaining rate greatly decreased. When mordenite

with the highest Cs<sup>+</sup> adsorption selectivity was added to the system of Cs-retaining vermiculite and 0.3 M KCl, the remaining rate of Cs<sup>+</sup> was 10%. Similarly, when Linde-type A with the highest Sr<sup>2+</sup> adsorption selectivity was added to the mixture of Sr-retaining vermiculite and 0.3 M KCl, the remaining rate of Sr<sup>2+</sup> was 4%. These means desorption rate or decontamination rate was 90% for Cs<sup>+</sup> and 96% for Sr<sup>2+</sup>.

The enhanced decontamination rate is ascribed to the coexistence of an adsorbent (zeolite) with a contaminated material (Cs- and Sr-retaining vermiculite) and an extracting solution (0.3 M KCl). When Cs- or Sr-retaining vermiculite was washed with 0.3 M KCl, some of the retained Cs<sup>+</sup> or Sr<sup>2+</sup> desorbed and released into the solution phase by cation exchange reaction with K<sup>+</sup>, and after reaching the equilibrium, the desorption of Cs<sup>+</sup> or Sr<sup>2+</sup> ended. In the system where mordenite coexisted with the mixture of Cs-retaining vermiculite and 0.3 M KCl, mordenite-adsorbed Cs<sup>+</sup> in the solution phase, the concentration of Cs<sup>+</sup> in solution decreased, and more Cs<sup>+</sup> released from vermiculite. The same occurred in the system of Sr<sup>2+</sup>. The coexistence of an adsorbent with a contaminated material such as soil and an extracting solution is effective for the decontamination of contaminated materials. In this case, the separation of the adsorbent and the contaminated material is essential. In this study, the separation was achieved by the wet sieving, because vermiculite (>150 μm) and zeolites (<90 μm) were successfully separated by using a 105-μm sieve. The separation method is important in the decontamination process of polluted materials, and some methods were proposed, one of them is magnetization of the adsorbents [52,53]. The development and utilization of the coexistence method by using effective and cheap adsorbents are desirable in the radioactive decontaminations in such areas as Fukushima, Japan.

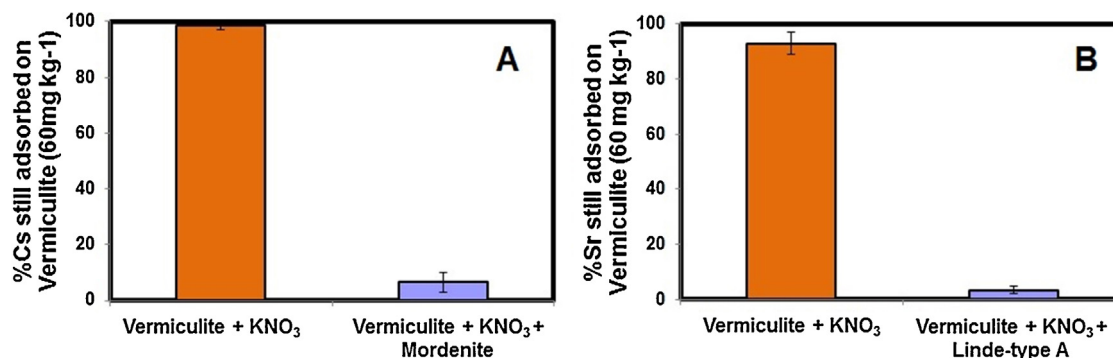


Fig. 3. Amount of Cs and Sr decontaminated from vermiculite. A: %Cs on vermiculite; B: %Sr on vermiculite.

#### 4. Conclusion

Mordenite had the highest Cs<sup>+</sup> adsorption selectivity, and Linde-type A had the highest Sr<sup>2+</sup> adsorption selectivity. The adsorption of Sr<sup>2+</sup> positively correlated to the CEC values of the zeolites, and Linde-type A with the highest CEC adsorbed more than 99% of Sr<sup>2+</sup> even in the presence of 0.5 M Na<sup>+</sup> and K<sup>+</sup>. In contrast, the CEC values of the zeolites did not relate to the adsorption selectivity of Cs<sup>+</sup>. The desorption of Cs and Sr from Cs- and Sr-retaining vermiculite by washing with 0.3 M KCl was enhanced by the coexistence of mordenite (Cs) and Linde-type A (Sr), and more than 90% of Cs and Sr desorbed from vermiculite.

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