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## Natural zeolites as potential materials for decontamination of radioactive cesium

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### Abstract

Adsorption experiments of Cs<sup>+</sup> were carried out by using two natural zeolites, namely mordenite and clinoptilolite. The same experiments were also conducted by using synthetic zeolite A, synthetic zeolite X, and artificial zeolite Na-P1 as references. The purpose of this study was to investigate the potential of natural zeolites on the adsorption of radioactive Cs<sup>+</sup>. The results indicated that although cation exchange capacity of the natural zeolites was much lower compared to the synthetic and artificial zeolites, the adsorption capacity of Cs<sup>+</sup> was much greater than the synthetic and artificial zeolites. The order of the adsorption capacity of Cs<sup>+</sup> was mordenite>clinoptilolite> Na-P1 >> zeolite A > zeolite X. It indicates that natural zeolites are promising materials in the removal of radioactive Cs<sup>+</sup>.

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*Keywords:* natural zeolites; adsorption; mordenite; clinoptilolite; cesium

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### 1. Introduction

A huge amount of radioactive <sup>137</sup>Cs and <sup>134</sup>Cs were released during the nuclear power plant accident in Fukushima, Japan, on March 11, 2011. Contaminations by the radioactive Cs occurred in land, rivers, forest, and

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plants. This is a very serious problem because the radioactive Cs is very dangerous for human body. Moreover, the problem will continue for a long period due to the long half-life of  $^{137}\text{Cs}$  which is 30.1 years. This means that after 30 years the amount of radioactive Cs will be only half. Many efforts have been made in order to solve the problem. One of them was to find effective adsorbents for  $^{137}\text{Cs}$ . Many adsorption experiments of  $\text{Cs}^+$  from aqueous system have been carried out using non-radioactive  $^{133}\text{Cs}$ , and part of the results are summarized by Division of Nuclear Fuel Cycle and Environment, Atomic Energy Society of Japan<sup>1</sup>.

Zeolites are natural and synthetic hydrated aluminosilicates having three dimensional frameworks. Along with the isomorphous replacement of Si by Al, negative charges are generated, and zeolites have a capacity to adsorb metal cations including heavy metal cations<sup>2,3</sup>. Commercially available synthetic zeolites with high purity are very expensive for the decontamination of radioactive Cs in the environment, but the prices of natural zeolites of mordenite and clinoptilolite types are very low. To decontaminate polluted environment by the radioactive Cs, it is necessary to concentrate the diffused radioactive Cs in waters, soils, and others onto adsorbents. For this purpose, low-cost natural zeolites are desirable.

In Japan, the polluted soils and wastes are planned to be kept in temporary storage facilities before being sent to the final disposal. However, the amount of the soils and wastes kept in the temporary storage facilities are increasing, and there is a need to reduce the amount of the soils and wastes. The adsorption and condensation of radioactive  $\text{Cs}^+$  by using adsorbents such as zeolite contributes the reduction of the soils and wastes needed to be kept, in addition to the decontamination of water and soil environments. In above cases, the separation of the zeolites from the mixture of zeolites and polluted materials is required, and for example, the magnetization of zeolites followed by separation using a magnet is proposed<sup>4,5</sup> for the purpose.

In this study, adsorption experiments of non-radioactive  $^{133}\text{Cs}$  were carried out by using two natural zeolites, namely mordenite and clinoptilolite. Synthetic zeolite A, zeolite X, and artificial zeolite Na-P1 were also used as references. Artificial zeolite Na-P1 was synthesized from coal fly ash. The purpose of this study was to investigate the potential of natural zeolites as an adsorbent of radioactive  $\text{Cs}^+$ , and to provide  $\text{Cs}^+$  selectivity of each zeolite species.

## 2. Materials and Methods

### 2.1. Materials

Five kinds of zeolite samples were used in this study. Two of them are natural zeolites, mordenite derived from Fukushima Prefecture, Japan and clinoptilolite from Shimane Prefecture, Japan. The other three zeolite samples were used as references, namely synthetic zeolite A (Linde type A), synthetic zeolite X, and zeolite Na-P1. Synthetic zeolite A and zeolite X were purchased from WAKO pure chemicals industry, Japan. Na-P1 was an artificial zeolite made from coal fly ash by mixing 10.0 g of coal fly ash with 80 mL of 2M NaOH, followed by heating at 100 °C for 24 h. The samples were saturated with  $\text{Na}^+$  in order to have  $\text{Na}^+$  as uniform exchangeable cation. The zeolite samples were characterized by powder X-ray diffraction (XRD) analysis by using a Rigaku Ultima IV X-ray diffractometer, with Cu-K $\alpha$  generated at 40kV and 40 mA, from 3°-60° of 2 $\theta$  angles with sampling width of 0.02° and sampling rate of 2° minute<sup>-1</sup>. Cation exchange capacity (CEC) was measured by initial saturation of the samples with 1 M KCl, followed by washing it with 80% ethanol. Finally, the  $\text{K}^+$  saturated samples were washed with 1 M  $\text{NH}_4\text{Cl}$  in order to extract the retained  $\text{K}^+$ , then the  $\text{K}^+$  in supernatant was measured by using an atomic absorption spectrophotometer (AAS, Hitachi Z-5000). CEC value was calculated from the amount of extracted  $\text{K}^+$  and was expressed in cmol (+) kg<sup>-1</sup>.

### 2.2. Adsorption experiments

Adsorption experiments of  $\text{Cs}^+$  were carried out in the presence of NaCl and  $\text{NH}_4\text{Cl}$  solutions. The experiments with NaCl simulated the adsorption of  $\text{Cs}^+$  from sea water, and the experiments with  $\text{NH}_4\text{Cl}$  was carried out supposing the adsorption of  $\text{Cs}^+$  after washing the polluted soils with salt solutions of  $\text{NH}_4^+$ . Various weights (0.1 g, 0.3 g, 1.0 g, 3.0 g, and 10.0 g) of each Na-saturated zeolite sample were mixed with 100 mL of 10 ppm Cs Clin 0.05 M NaCl solution. The mixtures were shaken for 24 h at room temperature, and then were centrifuged at 1600g for

10 min. The concentration of  $\text{Cs}^+$  of the supernatant (final  $\text{Cs}^+$  concentration) was measured by using AAS (Hitachi Z-5000). The amount of  $\text{Cs}^+$  adsorbed was calculated from the difference between the initial  $\text{Cs}^+$  concentration (10 ppm) and the final  $\text{Cs}^+$  concentration. The same experiments were carried out using 0.5 M NaCl, 0.05 M  $\text{NH}_4\text{Cl}$ , and 0.05 M  $\text{NH}_4\text{Cl}$  solutions instead of the 0.05 M NaCl solution.

### 3. Results and discussions

Characterization of the samples was done before the commencement of adsorption experiments. Figure 1 shows the powder XRD patterns of the zeolite samples. The five zeolite samples exhibited diffraction peaks that correspond to those in the literatures<sup>6,7</sup>. Table 1 illustrates the CEC values of the samples. Zeolite A was the sample with the highest CEC, and followed by zeolite X, Na-P1, mordenite, and clinoptilolite. The higher CEC of the synthetic zeolites (zeolite A and zeolite X) is due to the lower Si/Al ratios (around 1.0 to 1.2) and higher crystallinity, as shown in the XRD patterns of Fig. 1. On the other hand, the lower CEC of the natural zeolites is due to their higher Si/Al ratios and impurities contained. The Si/Al ratio of the natural mordenite and clinoptilolite is 4.88 and 5.04, respectively<sup>2</sup>.

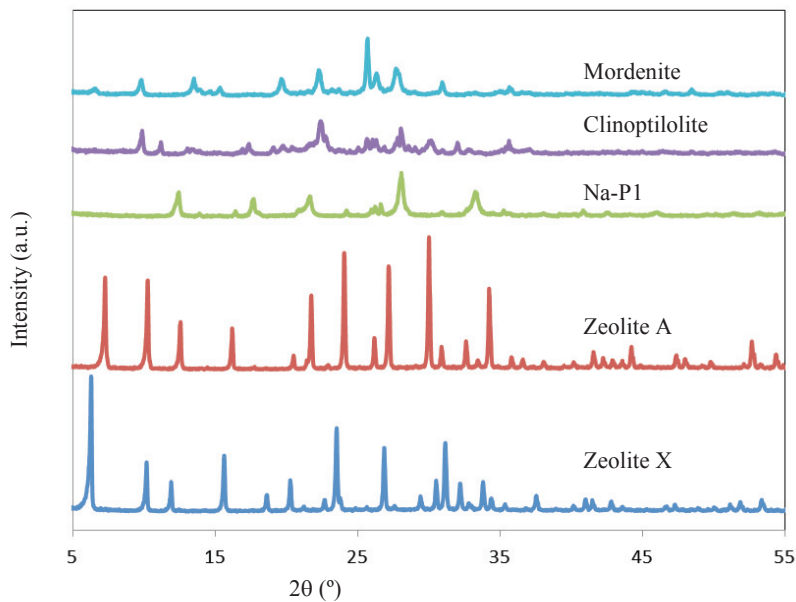


Fig. 1. Powder XRD patterns of the zeolite samples.

Table 1. CEC values of the zeolite samples.

Zeolite samples	CEC( $\text{cmol kg}^{-1}$ )
Mordenite	266
Clinoptilolite	211
Na-P1	325
Zeolite A	615
Zeolite X	556

Figure 2 shows adsorption isotherms of  $\text{Cs}^+$  of the zeolite samples in 0.05M NaCl (Fig. 2a) and in 0.5M NaCl (Fig. 2b). For all zeolite samples, the amounts of adsorption of  $\text{Cs}^+$  in 0.05 M NaCl were greater than those in 0.5M NaCl because the number of coexistent  $\text{Na}^+$  ions as a competitor was 10 times greater in 0.5 M NaCl than that in 0.05M NaCl. In the adsorption experiments of 10 ppm  $\text{Cs}^+$  in 0.05M NaCl, 0.075 mmol of  $\text{Cs}^+$  competed with 50 mmol of  $\text{Na}^+$ , or one  $\text{Cs}^+$  competed with more than 667  $\text{Na}^+$  to attach the surface of zeolites. In the case of adsorption of  $\text{Cs}^+$  in 0.5M NaCl, one  $\text{Cs}^+$  competes with more than 6667  $\text{Na}^+$ . The adsorption results indicated that  $\text{Cs}^+$  had much greater affinity to the surface of zeolites than  $\text{Na}^+$ . The order of the adsorption capacity and adsorption strength of the five zeolite samples was mordenite>clinoptilolite> Na-P1 >> zeolite A > zeolite X. Usually, adsorption of cations (cation exchange) or heavy metal ions on zeolite depend on the cation exchange capacity (CEC) value of zeolite. CEC values of the mordenite and clinoptilolite samples were 246 and 211 cmol  $\text{kg}^{-1}$ , respectively, much lower compared to those of the synthetic zeolite A and zeolite X (Table 1). This indicates that CEC is not a main factor affecting  $\text{Cs}^+$  adsorption. We considered that the adsorption of  $\text{Cs}^+$  is affected by the zeolite species or structure of zeolite rather than the CEC value.

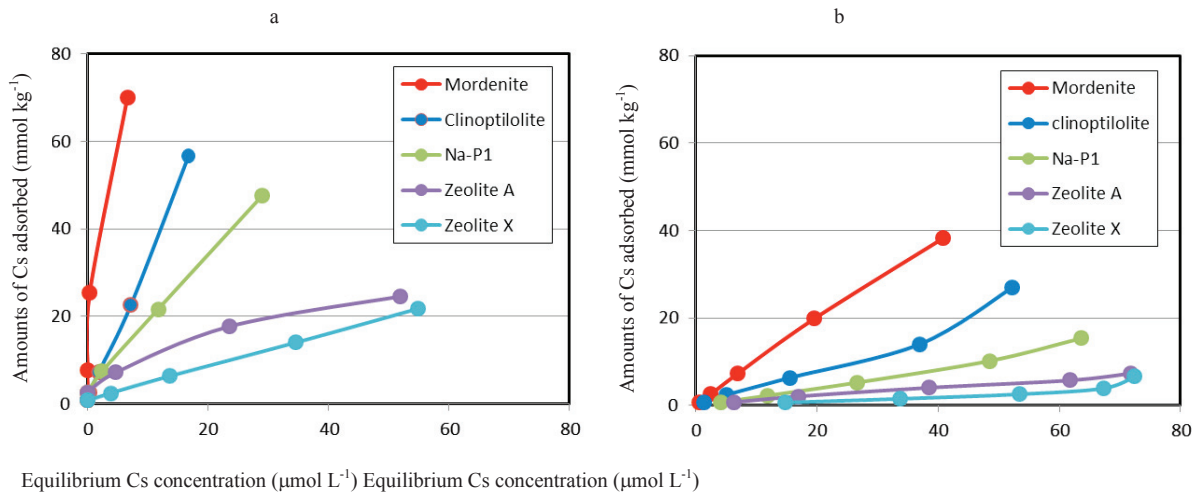


Fig. 2. (a) Cs adsorption isotherms in 0.05M NaCl; (b) Cs adsorption isotherms in 0.5M NaCl

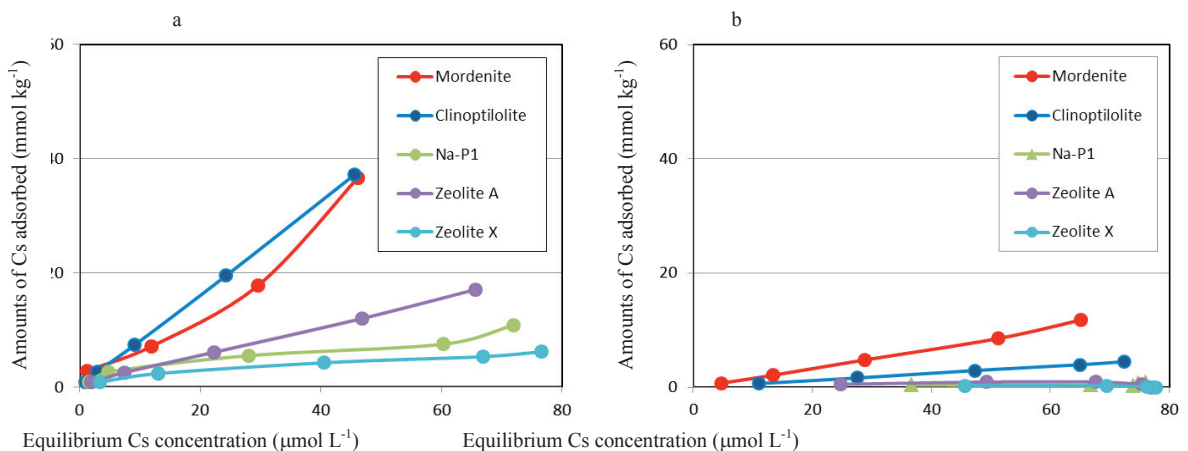


Fig. 3. (a) Cs adsorption isotherms in 0.05M  $\text{NH}_4\text{Cl}$ ; (b) Cs adsorption isotherms in 0.5M  $\text{NH}_4\text{Cl}$

Figure 3 shows adsorption isotherms of  $\text{Cs}^+$  of the zeolite samples in the presence of 0.05M  $\text{NH}_4\text{Cl}$  (Fig. 3a) and 0.5M  $\text{NH}_4\text{Cl}$  (Fig. 3b). In all cases, adsorption of  $\text{Cs}^+$  onto zeolites in  $\text{NH}_4\text{Cl}$  was lower as compared to the adsorption in  $\text{NaCl}$ . Here, relative ion replace ability or ease of ion removal from specific colloids, has been called lyotropic series, and they are in the order of  $\text{Li}^+ \approx \text{Na}^+ > \text{K}^+ \approx \text{NH}_4^+ > \text{Rb}^+ > \text{Cs}^+$ <sup>8</sup>. This result is in agreement with the lyotropic series, where  $\text{NH}_4^+$  is more difficult to be removed from colloids, in this case zeolite surface, than  $\text{Na}^+$ . In other words,  $\text{NH}_4^+$  is stronger competitor of  $\text{Cs}^+$  than  $\text{Na}^+$ . The order of Cs adsorption capacity and strength of the five zeolite samples were similar to the cases in  $\text{NaCl}$  above, with mordenite and clinoptilolite greater than the others.

The observations above indicate that within zeolite species, mordenite and clinoptilolite are excellent adsorbents of  $\text{Cs}^+$  in aqueous system. The higher selectivity may be ascribed to the presence of pores in zeolite structure with similar size to the diameter of  $\text{Cs}^+$  ion (ca. 3.6 Å). The two zeolite species used in this study were natural ones, and their prices are usually low. For example, the price of the natural mordenite in this study was about 0.3 USD  $\text{kg}^{-1}$ , much lower than the prices of synthetic zeolite A or zeolite X, which is about 50 US dollar  $\text{kg}^{-1}$ . Therefore, natural mordenite and clinoptilolite are favorable materials for the decontamination of radioactive Cs in aqueous system.

#### 4. Conclusions

Mordenite and clinoptilolite types of zeolites had high selectivity for  $\text{Cs}^+$  in aqueous solutions compared to synthetic zeolite A, zeolite X, and Na-P1, even in the presence of high concentrations of  $\text{Na}^+$  and  $\text{NH}_4^+$ . Natural samples of the two zeolite species are cheap. Therefore, they can be used for the decontamination of radioactive  $\text{Cs}^+$  from huge amounts of aqueous pollutants.

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