Cs$^+$ decontamination properties of mordenites and composite materials synthesized from coal fly ash and rice husk ash

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ABSTRACT
Mordenites were synthesized using the natural resource such as coal fly ash and rice husk ash. The Cs$^+$ adsorption rate (100 ppm Cs$^+$, 100 mL) in seawater for the prepared mordenite (1.0 g) was 83.2%. The Cs$^+$ adsorption rate for these mordenites almost depended on the calculated Cs$^+$ exchangeable value (mmol) using the cation exchange capacity (CEC) values. Composite powder materials consisting of mordenite and nanosized magnetite (Fe$_3$O$_4$) (10, 20, 30 wt%) were also synthesized from coal fly ash and rice husk ash. The total Cs$^+$ decontamination rates using the magnetic collection after the Cs$^+$ adsorption in water and seawater were ca. 90% and ca. 70% for the examined 20 wt% magnetite-containing composite material, respectively. Although the elution ratio of the Cs$^+$ ion was ca. 8% from all of the adsorbed Cs$^+$ by the dissolution test in slowly shaken deionized water for 14 days in the case of the Cs$^+$/adsorbed composite material (20wt% magnetite), the Cs$^+$ ion did not elute when the sample was heated at 100°C and higher temperature due to the Cs$^+$ containment in the glassy phase.

1. Introduction
The large amount of escaped Cs$^+$ radioisotopes from the accident at the Fukushima No.1 nuclear power plant due to the Great East Earthquake is an urgent problem [1,2]. The decontamination of these radioactive Cs$^+$ radioisotopes in ponds, sea, and fields is necessary for people to live without a health hazard. Materials having a high Cs$^+$ decontamination ability have been demanded for this purpose.

Zeolites are useful porous mineral aluminosilicates and widely used commercial adsorbents as ion-exchange materials for water purification and catalysts in the petrochemical industry [3,4]. The most promising characteristic of the zeolite is its highly selective Cs$^+$ adsorption ability coexisting with other ions in solution. There are various kinds of natural or artificial zeolites. In these zeolites, a Na-P1-type artificial zeolite (Na$_{8}$Al$_{12}$Si$_{23}$O$_{68}$$\cdot$12H$_2$O) synthesized from coal fly ash has a high Cs$^+$ ion adsorption ability and a high cation exchange capacity (CEC) value [5–8]. We evaluated the conditions for the Na-P1-type zeolite preparation and synthesized the composite material (magnetic zeolite) of the Na-P1-type zeolite and nanosized magnetite for the magnetic collection of the zeolite after the Cs$^+$ ion adsorption [9]. However, we found that the mordenite has the best Cs$^+$ adsorption selectivity among other zeolites, such as Na-P1, zeolite A, zeolite X, and clinoptilolite [10–12]. Based on these results, we focused on the mordenite (Na$_8$Al$_{12}$Si$_{23}$O$_{68}$$\cdot$24H$_2$O) synthesis. The preparation of artificial mordenite is necessary in order to improve the Cs$^+$ ion adsorption ability and to synthesize the composite material. In previous studies, the mordenite has been artificially synthesized from commercial chemical reagents or a natural raw material called diatomite [13–17]. In many cases, the mordenite has been prepared using a template agent, such as diethanolamine (DEA) and/or a seed powder of the same zeolite. Although the synthesis of mordenite has been reported by a hydrothermal method using the reagents of Na, Al, and Si sources without the template and the seed, the conditions for the preparation have not been established in detail [18,19]. We established the preparation method for the mordenite or the composite materials of mordenite and nanosized magnetite from the diatomite or chemical reagents [20,21]. The most suitable Al/Si ratio of the raw materials was determined for the preparation of the mordenite. In the case of the preparation from the chemical reagents, amorphous SiO$_2$ powder was necessary for the reaction using an NaOH solution. Based on these results, we considered the preparation of the mordenite from natural resources having a suitable Al/Si ratio using the combination of coal fly ash (high Al/Si ratio) and rice husk ash (low Al/Si ratio) at a low cost. It is well known that coal fly ash and rice husk are abundant by-products generated from a thermal power station or a rice milling factory, respectively. Furthermore, the preservation method for the zeolite containing radioactive Cs$^+$ is an important study [22]. We suggested the glass solidification method for the Cs$^+$ adsorbed zeolite by heat-treatment, because the zeolite is a glass formable Na$_2$O-Al$_2$O$_3$-SiO$_2$ systems [23].
Figure 1 shows an outline of this study. In this study, we synthesized the mordenite using the natural resources of coal fly ash and rice husk ash, and their composite materials of the mordenite and nanosized magnetite for the magnetic collection of the zeolite after the Cs\(^+\) ion adsorption. In addition, the elution ratio of the Cs\(^+\) ion was studied for the composite material and its heat-treated materials to immobilize the Cs\(^+\) in the decomposed zeolite.

2. Experimental

2.1. Preparation of mordenite

The mordenite was artificially synthesized using a combination of rice husk ash and coal fly ash without the addition of a template agent and a seed powder (Sample (a)). The rice husk ash was obtained by calcining rice husk at 700°C for 1 h in ambient air. This ash (2.0144 g) and NaOH (2.0 mol/L, 5.0 mL) were reacted by stirring for 30 min in a Teflon vessel. In another vessel, coal fly ash (1.226 g, JIS II type, Shikoku Electric Power Co., Japan) and an NaOH solution (2.0 mol/L, 5.0 mL) were reacted by stirring for 30 min, and then this suspension was added to the mixture of the rice husk ash suspension in a Teflon vessel with 5.9 mL of deionized water. In this mixture, the Al/Si ratio of the starting material was controlled at 0.125. This mixture was heated at 170°C for 24 h in an autoclave, and then washed several times by centrifugal separation with deionized water to remove the excess alkali. It was next dried at 70°C for 24 h. Another mordenite was also prepared using chemical reagents for as the control comparison (Sample (b)) [21].

2.2. Preparation of composite material containing mordenite and magnetite

Nanosized magnetite (Fe\(_3\)O\(_4\)) was prepared by the reverse coprecipitation method [24]. For the preparation of the magnetite, a stoichiometric ratio of FeCl\(_2\) · 4H\(_2\)O and FeCl\(_3\) · 6H\(_2\)O was dissolved in deionized water. An NaOH solution (6 mol/L) was placed in a hot water bath at 80°C. The mixed solution was then directly added to the NaOH solution with stirring and maintained at the same temperature for 1 h. The suspension of the synthesized magnetite was washed several times with hot water to remove the impurities, such as Na\(^+\) and Cl\(^-\) ions, resulting in a pH < 8.

For the composite material, the suspension of the magnetite was added to the mixture of the NaOH-reacted suspensions for the mordenite in an autoclave before heat-treatment. The mixture was well stirred, and then placed in the autoclave. The weight ratios of the 10-, 20-, and 30-wt% magnetite in the composite materials were controlled using the desired amount of the starting materials; that is, the mordenite and the nanosized magnetite suspension. The autoclave was heated at 170°C for 24 h. The synthesized powder was separated by centrifugal separation and washed several times with deionized water, and then dried at 70°C for 24 h.

2.3. Characterization

The samples were characterized by X-ray diffraction (XRD, Model Rint 2000, Rigaku Co.) (Cu-K\(\alpha\) radiation, 40 kV, 20 mA). The elemental ratio was analyzed by X-ray fluorescence (XRF, Model RIX2100, Rigaku Co.). The CEC of the samples was estimated by the K\(^+\) ion adsorption using a 1 M KCl solution. The K\(^+\) adsorbed materials were exchanged again with NH\(_4\)\(^+\) ions using a 1 M NH\(_4\)Cl solution. The CEC was determined by measurement of the K\(^+\) ion concentration in a desorbed and washed solution by atomic absorption spectrometry (ZA3300, Hitachi Co.).

For the measurement of the Cs\(^+\) adsorption ability, a 100 ppm Cs\(^+\) solution was prepared using CsCl (Wako Pure Chemical Ind., Ltd., 99.0% purity) and 100 mL of deionized water or seawater in a conical flask. We used natural seawater after filtration for this experiment. The

![Figure 1. Outline for this study.](image-url)
synthesized mordenite powder (1.0 g) was added to this solution and slowly shaken (Stroke: 4 cm, 1 Hz) for 1 h. After centrifugal separation, the Cs⁺ concentration in the solution was measured by atomic absorption spectrometry. Another Cs⁺ adsorption experiment was carried out at various amounts of samples (0.10, 0.25, 0.5, 1.0, 1.5, 2.0, and 4.0 g) in seawater for both mordenites using the same method.

The distribution coefficient was calculated according to the following equation using the Cs⁺ adsorption data at 298 K [25].

\[
K_d = \frac{V}{m} \cdot \frac{C_0 - C_e}{C_e}
\]

where \(K_d\) is the distribution coefficient (L/g), \(C_0\) and \(C_e\) are the activities of Cs⁺ in the initial and equilibrium solutions (mmol/L), respectively, \(V\) is the volume of the solution phase (L), and \(m\) is the mass of the artificial zeolite (g).

### 2.4. Magnetic collection rate for the composite material

After the Cs⁺ (100 ppm) adsorption of the composite material (1.0 g) in the water or seawater (100 mL) by shaking for 1 h, a neodymium magnet (14 mmφ × 5 mm, 3000 Gauss) was placed in the solution, and the mixture was then again slowly shaken for 2 h to collect the composite material using the magnet. The collected composite material was dried, and the magnetic collection rate, \(R_M\) (%), was calculated by the following Equation (2):

\[
R_M(\%) = \left( \frac{M_i}{M_f} \right) \times 100
\]

where \(M_i\) and \(M_f\) are the weights (g) of the initial sample and the sample collected by the magnet, respectively. The total Cs⁺ decontamination rate was calculated by multiplication of the Cs⁺ adsorption rate and the magnetic collection rate.

### 2.5. Cs⁺ elution test from the composite material

The composite material (1.0 g) of mordenite and magnetite (20 wt%) was utilized after the partial Cs⁺ (100 ppm) adsorption in the water (100 mL). The Cs⁺ adsorbed powder sample was heat-treated for 1 h in ambient air. The heat-treated composite material (0.1 g) was added to deionized water (10 mL) and slowly shaken (Stroke: 4 cm, 1 Hz) for 24 h at room temperature. After the centrifugal separation, the eluted Cs⁺ concentration of the separated solution was measured by atomic absorption spectrometry. The zeolite with the new deionized water (10 mL) was again shaken for 24 h, and the eluted ratio was repeatedly checked for a total of 14 times (14 days).

### 3. Results and discussion

#### 3.1. Preparation of the mordenite

Figure 2 shows the XRD results for coal fly ash and calcined rice husk for 1 h in ambient air at various calcination temperatures. Table 1 shows the elemental ratio of the natural resources for the coal fly ash and rice husk ash (calcined at 700°C). Quartz (SiO₂) and mullite (Al₂Si₂O₇) were confirmed in the coal fly ash (Figure 2). The Al/Si ratio of 0.435 was higher than that of the mordenite, and other elements were confirmed in the coal fly ash. For the rice husk ash, the amorphous phase (estimated from the “halo”) was obtained for the samples calcined at 600°C and higher temperatures. The cristobalite SiO₂ phase was also detected at 800°C and mainly formed at 900°C. For the rice husk ash, the main phase was the amorphous silica with potassium oxide as an impurity. The calcination temperature of 700°C was selected for the preparation of the rice husk ash, because amorphous SiO₂ powder was necessary for the reaction using the NaOH solution [21]. In this case, the yield of the rice husk ash was 15.7 wt% from the rice husk.

Figure 3 shows the XRD results of the sample prepared from (a) the combination of the coal fly ash and rice husk ash. The XRD result for the sample using (b) chemical regents was shown for comparison. The main peaks for the synthesized sample using the natural resources were the mordenite with mullite and quartz as the impurity phases from the unreacted coal fly ash. The peak intensity for the sample prepared using the chemical reagents was higher than that for the mordenite using the natural resources. Table 2 shows the elemental atomic ratio of the synthesized mordenites using natural resources and chemical reagents. The Al/Si ratio of the synthesized material was higher than that of the starting material (Al/Si = 0.125) and they agreed with the composition of the mordenite (Al/Si = 0.200) in all the samples. The non-reacted Si⁺ ions would remain in the solution after the reaction in the autoclave, but were removed by the washing process. However, the elements of Fe, Ca, K, and Mg from the natural resources remained in the synthesized samples. The peak position for the XRD results was not shifted for these samples. The CEC value for samples (a) and (b) was 165 and 184 cmol/kg, respectively. The CEC for the sample using the natural resources showed lower CEC values, which were influenced by the presence of the impurity phases. The CEC value for the samples was estimated by the K⁺ ion adsorption, and then exchanged with NH₄⁺ using a NH₄Cl solution. Although the elemental ratio for the alkali metals of Na⁺ and K⁺ decreased by the NH₄⁺ ion exchange, the other cations of Fe, Ca, and Mg had similar values. These cations, except for the alkali metals, would
mainly exist as isolated oxide phases with the mordenite. The peak intensity (Figure 3) for the mordenites was reduced for the impure cation containing samples (a), because these oxides might act to suppress the crystal growth of the mordenite.

3.2. Cs$^+$ adsorption selectivity for the synthesized mordenites

Table 3 shows the Cs$^+$ adsorption rate in the deionized water and seawater. The 100 ppm Cs$^+$ solution (100 mL) was adsorbed using the synthesized mordenite powder (1.0 g). The Cs$^+$ adsorption ratio in the water for both mordenites was >99%. The Cs$^+$ adsorption rate in seawater for the mordenites using the natural resources was 83.2%, which was lower than 89.3% for that using the chemical reagents. The decrease in the Cs$^+$ adsorption rate in seawater for both mordenites was due to the presence of cations in the seawater, such as Na$^+$ (10,500 ppm), Mg$^{2+}$ (1270 ppm), Ca$^{2+}$ (400 ppm), K$^+$ (380 ppm), etc., in which they acted as competitive ions. However, although the competitive ions in the seawater were considerably higher as compared to the

Figure 2. XRD results for coal fly ash and calcined rice husk for 1 h in ambient air for preparation of mordenite.

Table 1. Elemental atomic ratio of natural resources for preparation of mordenite.

| Element | Coal fly ash | Rice husk ash |
|---------|--------------|---------------|
| Si      | 1            | 1             |
| Al      | 0.435        | 0.001         |
| Na      | 0.0191       | 0.006         |
| Fe      | 0.0671       | 0.001         |
| Ca      | 0.0553       | 0.007         |
| K       | 0.0308       | 0.0631        |
| Mg      | 0.0322       | 0.008         |

Figure 3. XRD results for the samples prepared using (a) combination of coal fly ash and rice husk ash, and (b) chemical reagents.
Cs\(^+\) ion (100 ppm), the Cs\(^+\) adsorption rate for both mordenites was still high (more than 80%), indicating that the mordenites have a high selectivity to adsorb the Cs\(^+\) ion.

Figure 4 plots the effect of the amount of the synthesized sample powder on the Cs\(^+\) adsorption rate and distribution coefficient \((\log K_d)\) in seawater for the samples using (a) a combination of the coal fly ash and rice husk ash, and (b) chemical reagents. The Cs\(^+\) adsorption rate and distribution coefficient decreased with the decrease in the amount of the sample powder. Both values for sample (a) were lower than those for sample (b). For determination of the Cs\(^+\) adsorption rate, a 100 ppm Cs\(^+\) solution (100 mL) was calculated to contain \(7.524 \times 10^{-2}\) mmol Cs\(^+\). Based on the CEC value, the Cs\(^+\) adsorption ability for 1.0 g sample (a) (165 cmol/kg) was 1.65 mmol Cs\(^+\). In this case, the calculated Cs\(^+\) exchange ratio was ca. 4.6% in all of the cation sites as a monovalent alkali ion from the CEC value. The absolute Cs\(^+\) exchangeable value can be calculated using the following equation:

\[
\text{Cs}^+ \text{exchangeable value (mmol)} = \text{CEC(cmol/kg)} \times m \times 10^{-2}
\]  

where \(m\) is the weight (g) of the samples. The Cs\(^+\) adsorption rate in seawater was studied when the sample weight \(m\) was changed for the (a) and (b) samples. Table 4 lists these results. Figure 5 shows the relationship between the calculated Cs\(^+\) exchangeable value and Cs\(^+\) adsorption rate in seawater for the (a) and (b) samples. Although the Cs\(^+\) adsorption ability for the (a) sample was slightly lower than that of the (b) sample, the Cs\(^+\) adsorption rate almost agreed with the calculated Cs\(^+\) exchangeable value.

### 3.3. Composite material containing the mordenite and nanosized magnetite

The mordenite-magnetite composite material is one of the suitable candidates for the Cs\(^+\) decontamination from water and soils. The composite material of the artificial mordenite and nanosized magnetite using the coal fly ash and rice husk ash was synthesized for the collection after the Cs\(^+\) adsorption. Figure 6 shows the XRD results of the mordenite using the combination of the coal fly ash and rice husk ash, and the composite materials (magnetite of 10, 20, 30 wt%). The peaks for the magnetite with the mordenite were confirmed for the composite materials. The peak intensity of the mordenite decreased with the increase in the magnetite content. Figure 7 shows the relationship between the magnetite content and the Cs\(^+\) adsorption rate. For the Cs\(^+\) adsorption ability, the Cs\(^+\) adsorption in the water retained a high (>99%) adsorption ability for all the composite samples. Although the Cs\(^+\) adsorption in the seawater decreased with the increase in the magnetite content, the composite material maintained a high selectivity for the Cs\(^+\) ion in seawater.

| Sample (a) | Sample (b) |
|------------|------------|
| Weight (g) | Cs\(^+\) exchangeable value (mmol) | Cs\(^+\) adsorption rate in seawater | Cs\(^+\) exchangeable value (mmol) | Cs\(^+\) adsorption rate in seawater |
| 0.10       | 0.165      | 27.22      | 0.184       | 30.75      |
| 0.25       | 0.412      | 54.26      | 0.460       | 60.42      |
| 0.50       | 0.825      | 73.41      | 0.920       | 77.26      |
| 1.00       | 1.650      | 83.20      | 1.840       | 89.30      |
| 1.50       | 2.475      | 90.43      | 2.760       | 91.84      |
| 2.00       | 3.300      | 92.86      | 3.680       | 94.27      |
| 4.00       | 6.600      | 97.00      | 7.360       | 98.30      |
Figure 8 shows the results of the Cs⁺ adsorption rate in water (Figure 7), the magnetic collection rate, and the total Cs⁺ decontamination ability for the composite materials (10, 20, 30 wt%). After the Cs⁺ adsorption in the water, the composite material was collected by a neodymium magnet. The Cs⁺ adsorption rate in the water was a consistently high value (>99%) for all the composite materials. The magnetic collection rate increased with the increase in the magnetic content and was greater than 90% for the 20 and 30 wt% magnetite-containing samples. The total Cs⁺ decontamination rate was highly dependent on the magnetic collection rate. The total Cs⁺ decontamination rates by the magnetic collection after the Cs⁺ adsorption in water were also greater than 90% for the 20 and 30 wt% magnetite-containing composite materials. Figure 9 shows the total decontamination rates in water and seawater for the composite samples. For the decontamination in water, the high
decontamination rate was possible for the composite samples using natural sources with the higher magnetite content. In seawater, the decontamination rate was ca. 70% for the samples using natural sources.

3.4. Elution test for the heat-treated composite samples

Figure 10 shows the XRD results for the heat-treated composite material of the mordenite and the magnetite (20 wt%) at various temperatures for 1 h in ambient air. The XRD peaks of the mordenite phase were maintained for the sample heated at 600°C, but it almost disappeared at 800°C. A glassy amorphous phase was confirmed as the “halo” at around 2θ = 20°–25° for the samples calcined at 800°C and higher temperatures. The mordenite was completely decomposed and the magnetite (Fe₃O₄) was oxidized to hematite (Fe₂O₃) by the heat-treatment at 900°C at ambient air. A quartz...
(SiO₂) phase was dissolved in the Na₂O-Al₂O₃-SiO₂ glassy phase at 1000°C and higher temperatures to make SiO₂-rich glassy phase. Figure 11 shows an SEM observation for the heated composite materials of the mordenite and the magnetite (20 wt%) at various temperatures for 1 h in ambient air. The particles of the magnetite in large mordenite were shown in the TEM observation for the No-treated sample. The particle size of the magnetite was ca. 10–20 nm. The particle growth was not observed by the heat-treatment even at 900°C. Particles were vitrificated to obtain a smooth surface by the heat treatment at 1000°C and higher temperatures.

Figure 12 shows the change in the accumulated Cs⁺ elution ratio in deionized water for the heated samples for 14 days. The non-heated sample showed a continuous Cs⁺ elution to ca. 8% from all of the adsorbed Cs⁺ for 14 days. The Cs⁺ elution decreased with the heat-treated temperature and it did not elute from the sample heated at 1000°C or higher to immobilize the Cs⁺ in the decomposed zeolite. The formation of the glassy phase would act to fix the Cs⁺ ion and to reduce the surface area. This heat-treatment method is very effective for the preservation of the zeolite containing a low-level radioactivity.

4. Conclusion

Mordenite has been evaluated as the most suitable adsorbent for radioactive Cs⁺ decontamination due to its high selectivity of the Cs⁺ ion. The mordenites were artificially synthesized using the natural resource combination of low-cost coal fly ash and rice husk ash. The Cs⁺ adsorption ability in seawater for the mordenites prepared using the natural resources was slightly lower than that of the mordenite prepared using chemical reagents. This difference in the ability was due to the difference in the Cs⁺ exchangeable value, which was calculated using the CEC value. The total Cs decontamination rates of 90% in water and ca. 70% is sufficient for the composite material using low-cost natural resources. After the magnetic collection of the Cs⁺ decontaminated composite material, the heat-treatment for the zeolite decomposition at 1000°C was very effective for their preservation.

Disclosure statement

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magnetite from diatomites for radioactive Cs decontamination. J Ceram Soc Jpn. 2015;123:129–135.

[21] Aono H, Kaji N, Itagaki Y, et al. Synthesis of mordenite and its composite material using chemical reagents for Cs decontamination. J Ceram Soc Jpn. 2016;125:617–623.

[22] Wu Y, Zhang X, Wei Y, et al. Development of adsorption and solidification process for decontamination of Cs-contaminated radioactive water in Fukushima through silica-based AMP hybrid adsorbent. Separation Purif Technol. 2017;181:76–84.

[23] Aono H, Takahashi R, Itagaki Y, et al. Cs immobilization using the formation of the glassy phase by the heat-treatment of natural mordenite. J Nucl Mater. 2018;508:20–25.

[24] Aono H, Hirazawa H, Naohara T, et al. Synthesis of fine magnetite powder using reverse coprecipitation method and its heating properties by applying AC magnetic field. Mater Res Bull. 2005;40:1126–1135.

[25] Khan SA, Reman RU, Khan MA. Adsorption of Cs(I), Sr(II) and Co(II) on Al₂O₃. J Radioanalytical Nucl Chem. 1995;190:81–96.