Preparation of mordenite and its composite material with nano-sized magnetite from diatomites for radioactive Cs decontamination

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Mordenite was artificially synthesized using various diatomites for radioactive Cs decontamination. A high CEC (Cation Exchange Capacity) value was obtained when the diatomite had a high Al/Si elemental ratio. The Cs⁺ adsorption rate from 100 ppm Cs solution for the synthesized mordenite (1.0 g) was ca. 100% and ca. 83% in 100 mL of water and seawater, respectively. The composite powder material consisting of mordenite and nano-sized magnetite was synthesized from a mixed slurry of the diatomite and nano-sized magnetite. Magnetic collection rate for the composite material using a neodymium magnet was larger than 90% for the 20 and 30 wt % magnetite-containing composite materials. The total Cs decontamination rates using magnetic collection after the Cs⁺ adsorption in water were 92.7% and 97.2% for the 20 and 30 wt % magnetite-containing composite material, respectively.

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1. Introduction

The accident at the Fukushima No.1 nuclear power station has caused contamination by radioactive materials including 134Cs and 137Cs in the environment. Decontamination of these radionuclides has been required for suppression of human radiation exposure. In particular, the radioactive Cs exists in an adsorbed state in the soils. Various materials have been considered as an absorbent for the Cs decontamination, namely active carbon, Prussian blue and zeolites.

Zeolite is known as an alkali aluminosilicate having various nano-sized pores in its crystalline structure with cation exchange ability. Many kinds of zeolites such as chabazite, clinoptilolite and mordenite exist in nature, and they have been used for adsorption of heavy metals in liquid waste and for decontamination of high 137Cs activity level water at Three Mile Island. However, for radioactive Cs decontamination in the soil, the zeolite powder can’t be collected after the Cs⁺ adsorption. In our previous study, we synthesized a composite material of Na-P1-type zeolite (synthesized from fly-ash) and magnetite for the magnetic collection. Decontamination of the soil containing radioactive Cs was possible using this composite material.

Among the various zeolites, the mordenite (Na₈Al₈Si₄₀O₉₆·2₄H₂O) has a high selectivity for Cs⁺ ion. The synthesis of mordenite has been reported by a hydrothermal method using reagents of Na, Al and Si sources. Among the various raw materials, diatomite has been reported for the synthesis of artificial mordenite at low cost without the addition of a template or a seed. Furthermore, preparation of a composite material of artificial mordenite and magnetite also seems possible by using our method.

In this study, we investigated the synthesis conditions of the mordenite from various diatomites as raw materials and the composite material of the mordenite and the magnetite.

2. Experimental procedure

2.1 Synthesis of artificial mordenite

In this study, six kinds of diatomites, (a) Wako Pure Chemical Ind., Ltd. (b) Hayashi Pure Chemical Ind., Ltd. (c) collected natural minerals from Toyama prefecture, Japan, (d) Kishida Chemical Co., Ltd. (e) Kanto Chemical Co., Ltd. (f) Nacalai Tesque, Inc. were used for the preparation of the mordenite. The diatomite powder (5 g) and NaOH solution (1 mol/L, 22.5 mL) were mixed and put in an autoclave (inside: Teflon vessel; outside: stainless steel, Sanai Science Co., Ltd.). This autoclave was pre-heated at 70°C for 6 h and then heated at 170°C for 72 h. After the heating treatment, the synthesized powder was separated by centrifugal separation several times with deionized water to remove excess alkali, and then it was dried at 70°C for 24 h. Natural mordenite (Iizaka mine, Nitto Funka Co.) was utilized for a comparison sample.

2.2 Synthesis of composite material

Figure 1 shows the flow chart of preparation for the composite material of mordenite and magnetite. Nano-sized magnetite was prepared by the reverse coprecipitation method. For preparation of the magnetite, a stoichiometric ratio of FeCl₃·4H₂O and FeCl₃·6H₂O were dissolved in deionized water. NaOH solution (6 mol/L) was placed in a hot water bath at 80°C. The mixed solution was then directly dropped into 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 up to pH<8. For the composite material, the suspension of the magnetite was mixed with the (a) Wako diatomite and was added to NaOH solution (1 mol/L). The mixtures were mixed well and put in the autoclave. The weight ratio for 10-, 20-, 30-wt%...
30 wt\% magnetite in the composite materials was controlled by using the desired amount of the starting materials of the diatomite and the nano-sized magnetite suspension. The amount of the NaOH solution (mL) depended on the diatomite content. The autoclave was heated at 170°C for 24 h. The synthesized powder was separated and washed with deionized water by centrifugal separation several times and then was dried at 70°C for 24 h.

2.3 Cs\(^+\) adsorption rate

A 100 ppm Cs\(^+\) solution (100 mL) was prepared using CsCl in deionized water and seawater (sampled in Matsuyama city, Ehime prefecture, Japan). The seawater was diluted with water so as to give each seawater concentration of 1, 10, 50, 100%. The 100 mL of Cs\(^+\) solution was added to 1 g of the mordenite powder, then centrifugation was done, and the mixture was then shaken slowly (1 Hz) for 1 h. After the Cs\(^+\) adsorption, the Cs\(^+\) concentration of the centrifuged solution was measured using atomic absorption spectrometry (Z-5000, Hitachi Co.). The Cs\(^+\) adsorption rate \(R_C(\%)\) was calculated by the following Eq. (1):

\[
R_C(\%) = \left( \frac{C_i - C_f}{C_i} \right) \times 100 \tag{1}
\]

where \(C_i\) (100 ppm) and \(C_f\) are the Cs\(^+\) concentrations of the initial solution and that after adsorption, respectively.

2.4 Magnetic collection rate for the composite material

Figure 2 shows the experimental procedure of the magnetic collection method. After the Cs adsorption in the water, a neodymium magnet (14 mm\(\times\)5 mm, 3000 Gauss) was put into the solution, and the mixture was then shaken slowly for 2 h to collect the composite material. The collected composite material was dried, and the magnetic collection rate \(R_M(\%)\) was calculated by the following Eq. (2):

\[
R_M(\%) = \left( \frac{M_i}{M_f} \right) \times 100 \tag{2}
\]

where \(M_i\) and \(M_f\) are the weights (g) of the initial sample and the sample collected by the magnet, respectively. The increase in the weight for the magnetic mordenite due to the Cs\(^+\) exchange was smaller than 0.01 g (1.0%).

2.5 Characterization

All samples were characterized by X-ray diffraction (XRD, Model Rint 2000; Rigaku Co., using Cu-K\(\alpha\) radiation). The elemental ratio for the diatomites and the synthesized zeolites was analyzed by X-ray fluorescence (XRF, Model RIX2100, Rigaku Co.). The cation exchange capacity (CEC) of the synthesized zeolites was estimated from the K\(^+\) ion exchange ability using KCl solution (1 mol/L). The adsorbed K\(^+\) was then extracted with NH\(_4\)\(^+\) ions, using NH\(_4\)Cl solution (1 mol/L). The CEC was determined by the measurement of the total amount of K\(^+\) ion extracted using atomic absorption spectrometry (Z-5000, Hitachi Co.).

3. Results and discussion

3.1 Preparation of the mordenite from various diatomites

Diatomites are natural sedimentary rocks, and their typical chemical composition is 80 to 90% silica with several % of alumina in clay minerals and other oxides such as iron oxide. The elemental ratio in the XRF results for each diatomite is listed in Table 1. The elemental ratio was different for all the diatomites. Wako diatomite had the highest Al/Si ratio of all the diatomites. Figure 3 shows the XRD results for each diatomite. The XRD pattern was arranged in order of the Al/Si ratio of the diatomites. Each diatomite contained different crystalline phases such as quartz, cristobalite, metahalloysite, anorthite and an amorphous phase and various unknown impurities. The (a) Wako diatomite showed the highest Al/Si ratio in the XRF results and was free of...
the quartz in the XRD results. Figure 4 shows the XRD results of the mordenites synthesized from each diatomite by pre-heating at 70°C for 6 h and heating at 170°C for 72 h. The XRD result for a natural mordenite (Iizaka mine, Nitto Funka Co.) is shown in the figure for comparison. The mordenite phase was confirmed for all the synthesized materials from the diatomites. The quartz phase was confirmed for all the samples except for that from (a) Wako diatomite, because the stable quartz in each diatomite was not dissolved by the reaction with the NaOH solution in the autoclave. High purity mordenite having a high Al/Si ratio with few impurities was synthesized from the (a) Wako diatomite. In all cases, the Al/Si ratio of the synthesized mordenite was higher than that of the raw material. Figure 5 shows the relationship

Table 1. The elemental ratio in XRF results for each diatomite

| Element | (a) Wako | (b) Hayashi | (c) Toyama | (d) Kishida | (e) Kanto | (f) Nacalai |
|---------|----------|-------------|------------|------------|----------|------------|
| Si      | 1        | 1           | 1          | 1          | 1        | 1          |
| Al      | 0.125    | 0.123       | 0.099      | 0.093      | 0.070    | 0.029      |
| Na      | 0.031    | 0.013       | 0.034      | 0.009      | 0.021    | 0.048      |
| K       | 0.023    | 0.024       | 0.024      | 0.018      | 0.013    | 0.007      |
| Ca      | 0.032    | 0.016       | 0.007      | 0.007      | 0.006    | 0.003      |
| Fe      | 0.032    | 0.023       | 0.018      | 0.013      | 0.014    | 0.010      |
between the Al/Si ratio and the CEC values for the mordenites prepared from various diatomites. The theoretical CEC of the mordenite (Na₈Al₈Si₄₀O₉₆·2₄H₂O) calculated from the molecular weight was 229 (cmol/kg). The maximum CEC of 172 (cmol/kg) was obtained for the mordenite synthesized from (a) Wako diatomite, which was ca.75% compared with the theoretical CEC. This CEC value of the synthesized mordenite was very close to that of the natural mordenite. The CEC value would be influenced by the amount of impurities in the mordenite, because the Al/Si ratio of 0.229 for the natural mordenite was close to the theoretical 0.200. The CEC value decreased with a decrease in the Al/Si ratio in the mordenite. The number of cation exchange sites was influenced by the negative charge with the decrease in Al/Si ratio in the mordenite. From these results, we decide to utilize the (a) Wako diatomite as the most suitable raw material for the synthesis of mordenite in this study.

### 3.2 The synthesis conditions of mordenite from diatomite

Table 2 shows the synthesized products and the CEC values for the materials under various conditions using the (a) Wako diatomite as raw material.

| Sample number | NaOH concentration (mol/L) | Pre-heating (With or Without) | Heat-treatment temperature (°C) | Heat-treatment time (h) | Synthesized products | CEC (cmol/kg) |
|---------------|-----------------------------|------------------------------|-------------------------------|------------------------|---------------------|---------------|
| 1             | 0.3                         | With                         | 170                           | 72                     | M+A                 | 160           |
| 2             | 0.5                         | With                         | 170                           | 72                     | M+U                 | 161           |
| 3             | 1                           | With                         | 170                           | 72                     | M+A                 | 172           |
| 4             | 2                           | With                         | 170                           | 72                     | M+Q                 | 144           |
| 5             | 4                           | With                         | 170                           | 72                     | M+Q+A               | 133           |
| 6             | 1                           | With                         | 150                           | 24                     | D                   | 144           |
| 7             | 1                           | With                         | 160                           | 24                     | M                   | 176           |
| 8             | 1                           | With                         | 170                           | 24                     | M                   | 179           |
| 9             | 1                           | With                         | 180                           | 24                     | M+A                 | 169           |
| 10            | 1                           | With                         | 170                           | 3                      | D                   | 147           |
| 11            | 1                           | With                         | 170                           | 6                      | M                   | 171           |
| 12            | 1                           | With                         | 170                           | 12                     | M                   | 181           |
| 13            | 1                           | With                         | 170                           | 48                     | M+A                 | 159           |
| 14            | 1                           | Without                      | 170                           | 3                      | D                   | 136           |
| 15            | 1                           | Without                      | 170                           | 6                      | D                   | 166           |
| 16            | 1                           | Without                      | 170                           | 12                     | M+A                 | 172           |
| 17            | 1                           | Without                      | 170                           | 24                     | M+A                 | 173           |
| 18            | 1                           | Without                      | 170                           | 48                     | M+A                 | 165           |
| 19            | 1                           | Without                      | 170                           | 72                     | M+A                 | 171           |

Synthesized product (M, mordenite; A, Analcime; Q, quartz; D, diatomite; U, unknown).

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Fig. 6. The XRD results for mordenites prepared from (a) Wako diatomite using various concentrations of NaOH solution at 170°C for 72 h.

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#### Table 2. The synthesized products and the CEC value for the materials under various conditions using the (a) Wako diatomite as raw material

| Sample number | NaOH concentration (mol/L) | Pre-heating (With or Without) | Heat-treatment temperature (°C) | Heat-treatment time (h) | Synthesized products | CEC (cmol/kg) |
|---------------|-----------------------------|------------------------------|-------------------------------|------------------------|---------------------|---------------|
| 1             | 0.3                         | With                         | 170                           | 72                     | M+A                 | 160           |
| 2             | 0.5                         | With                         | 170                           | 72                     | M+U                 | 161           |
| 3             | 1                           | With                         | 170                           | 72                     | M+A                 | 172           |
| 4             | 2                           | With                         | 170                           | 72                     | M+Q                 | 144           |
| 5             | 4                           | With                         | 170                           | 72                     | M+Q+A               | 133           |
| 6             | 1                           | With                         | 150                           | 24                     | D                   | 144           |
| 7             | 1                           | With                         | 160                           | 24                     | M                   | 176           |
| 8             | 1                           | With                         | 170                           | 24                     | M                   | 179           |
| 9             | 1                           | With                         | 180                           | 24                     | M+A                 | 169           |
| 10            | 1                           | With                         | 170                           | 3                      | D                   | 147           |
| 11            | 1                           | With                         | 170                           | 6                      | M                   | 171           |
| 12            | 1                           | With                         | 170                           | 12                     | M                   | 181           |
| 13            | 1                           | With                         | 170                           | 48                     | M+A                 | 159           |
| 14            | 1                           | Without                      | 170                           | 3                      | D                   | 136           |
| 15            | 1                           | Without                      | 170                           | 6                      | D                   | 166           |
| 16            | 1                           | Without                      | 170                           | 12                     | M+A                 | 172           |
| 17            | 1                           | Without                      | 170                           | 24                     | M+A                 | 173           |
| 18            | 1                           | Without                      | 170                           | 48                     | M+A                 | 165           |
| 19            | 1                           | Without                      | 170                           | 72                     | M+A                 | 171           |

Synthesized product (M, mordenite; A, Analcime; Q, quartz; D, diatomite; U, unknown).
170°C without pre-heating at 70°C for 6 h (samples 14–19). In comparison with Fig. 8 and in the case of no pre-heating, a heat treatment time of 12 h was needed for formation of the mordenite. However, a small amount of analcime in the absence of pre-heating was confirmed for all the samples. Figure 10 shows the relationship between heat-treatment time and the CEC values for mordenites with and without pre-heating. The CEC values were close. From these results, we decided that a suitable and simple heat-treatment condition is at 170°C for 24 h without pre-heating as for the sample 17.

Figure 11 shows the relationship between the concentration of the seawater and Cs\(^+\) adsorption rate for mordenite prepared from (a) Wako diatomite and a natural mordenite.
% in water for both mordenites. The Cs\(^+\) adsorption rate decreased with an increase in the concentration of the seawater. Furthermore, a high selectivity for Cs\(^+\) ion of ca. 83% was observed even in the seawater. The Cs\(^+\) adsorption rate of artificial mordenite was almost the same as that of the natural mordenite.\(^6\) For radioactive Cs decontamination, superior adsorption was selectively confirmed for the artificial mordenite.

### 3.3 Preparation of the composite material

The synthesis condition of the sample number 17 was adopted for the synthesis of the composite material of artificial mordenite and nano-sized magnetite. Figure 12 shows the XRD results of the artificial mordenite (sample 17) and the composite materials (magnetite 10, 20, 30 wt%). The peaks of the magnetite were confirmed and their intensity increased with the increase in the magnetite content. The peak intensity of mordenite was decreased by the existence of the magnetite. Table 3 shows the XRF results for the elemental ratio of the artificial mordenite and the composite materials (10, 20, 30 wt%). The chlorine from the starting material of the magnetite was hardly detected in the composite material, indicating that various processes were complete. The Fe content gradually increased with the increase in the magnetite content in the composite material.

Figure 13 shows the relationship between the magnetite content (wt%) and the CEC value of the composite materials. The CEC value proportionally decreased with the increase in the amount of magnetite. The existence of the magnetite nanoparticles in the composite material monotonically influences the numbers of the Cs\(^+\) adsorption sites of the mordenite. Figure 14 shows FE-SEM images of (a) artificial mordenite and (b) the composite materials (20 wt%). The shape of the mordenite was the concentrated needles as the primary particle.\(^13,19\) The dispersed nano-sized magnetite particles were observed on the surface of the mordenite in the (b) composite sample. Figure 15 shows the Cs\(^+\) adsorption rate in water and seawater for the artificial mordenite and the composite materials (10, 20, 30 wt%). The Cs\(^+\) adsorption rate in water was 98.6–99.0%. The Cs\(^+\) adsorption rate in seawater was

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**Table 3.** The XRF results for elemental ratio of each artificial mordenite and the composite materials (10, 20, 30 wt%)

| Element (mol) | Artificial mordenite | 10 wt% | 20 wt% | 30 wt% |
|--------------|----------------------|--------|--------|--------|
| Si           | 1                    | 1      | 1      | 1      |
| Al           | 0.190                | 0.183  | 0.180  | 0.190  |
| Na           | 0.150                | 0.165  | 0.239  | 0.183  |
| K            | 0.032                | 0.031  | 0.027  | 0.030  |
| Ca           | 0.046                | 0.041  | 0.033  | 0.040  |
| Fe           | 0.043                | 0.163  | 0.287  | 0.495  |

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![Fig. 12. The XRD results for the artificial mordenite and the composite materials (10, 20, 30 wt%).](image)

![Fig. 13. The relationship between CEC value and magnetite content (wt%) of the artificial mordenite and the composite materials (10, 20, 30 wt%).](image)

![Fig. 14. FE-SEM images of (a) artificial mordenite and (b) composite material (20 wt%).](image)

![Fig. 15. The Cs\(^+\) adsorption rate in water and seawater for the artificial mordenite and the composite materials (10, 20, 30 wt%).](image)
also a high value and gradually decreased with the increase in the magnetite content of the composite materials. The existence of the magnetite did not strongly influence the Cs\(^+\) adsorption of the mordenite. The Cs\(^+\) adsorption rate in water or seawater depended on the ability of the zeolites. This ability was hardly influenced by the decrease in the zeolite content with an increase in magnetite content, because enough numbers of Cs\(^+\) adsorption sites remained in the magnetic containing zeolites for the 100 ppm Cs\(^+\) solution (100 mL). Figure 16 shows the results of the magnetic collection rate, the Cs\(^+\) adsorption rate in water (Fig. 14), and the total Cs decontamination of the composite materials (10, 20, 30 wt%). The magnetic collection rate was larger than 90% for 20- and 30 wt% magnetite-containing samples. This means that the magnetite was tightly connected to the mordenite to form the composite material. The majority of the magnetite particles might exist between the needle-type mordenites. The Cs\(^+\) adsorption rate in water was a constant value for all the composite materials. The total Cs decontamination rate highly depended on the magnetic collection rate. The total Cs decontamination rates using magnetic collection after Cs\(^+\) adsorption in water were 92.7 and 97.2% for the 20- and 30 wt% magnetite-containing composite material, respectively. From these results, the magnetite-mordenite composite material is one of the suitable candidates for Cs decontamination.

4. Conclusion

We synthesized the mordenites using six kinds of diatomites as raw materials. The CEC (Cation Exchange Capacity) value for the synthesized mordenites depended on the Al/Si ratio of the diatomite. The Cs\(^+\) adsorption rates of the artificial mordenite were ca. 100% and ca. 83% in water and in seawater, respectively. Furthermore, the composite materials were synthesized from a mixed solution of the diatomite and nano-sized magnetite. Although the nano-sized magnetite was dispersed on the surface of the mordenite as shown by FE-SEM for the composite materials, the magnetic collection rate using a neodymium magnet in solution was larger than 90% for the composite material (20- and 30 wt%). These results prove that Cs decontamination is possible using the mordenite-magnetite composite material.

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