Adsorption/Desorption Characteristics of Cesium Ions on Natural and Synthetic Minerals

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Abstract

Geochemical reference samples, a natural zeolite, synthetic zeolites, vermiculite, and bentonite were tested for their adsorption and desorption characteristics of cesium. Large amounts of cesium were adsorbed on bentonite and natural zeolite because of their pore sizes or lamellar structures and their large numbers of exchangeable cations. In the geochemical reference samples, the adsorption behavior of cesium was affected by the exchangeable cation content and the soil corrosion product content. The desorption ratios of cesium from the minerals were influenced by the amounts of cations in the solution. The desorption ratios of cesium from the natural and synthetic zeolites were 5.4% and 70% to 75%, respectively, with 0.1 mol/L of hydrochloric acid. The amounts of aluminum ions eluted from the synthetic zeolites due to structure collapse was approximately 30-fold higher than that from the natural zeolite. Cesium adsorption ratios onto the minerals and the desorption ratios from the minerals decreased as the calcination temperature increased. X-ray diffraction and scanning electron microscopy confirmed that the mineral surface was melted by heating. The desorption of cesium ions was inhibited by cement hardening treatment of the minerals because the cement hydrates that coated the mineral particle surfaces could adsorb cesium.

Keywords: Cesium, Lamellar silicate compound, Calcination treatment, Cement hardening

1. Introduction

There are many types of minerals possessing unique structures and characteristics. For example, zeolites have three-dimensional network structures; also, some soil minerals categorized as silicates have lamellar structures [1-9]. These minerals show differences in their adsorption of exchangeable cations on the surfaces of their mineral skeletons; they also have different adsorption sites. Additionally, weathering processes such as erosion cause structural and chemical changes in natural minerals. Consequently, the adsorption of ions onto natural minerals is a complicated process that is affected by many factors.

This study aims to research the establishment of a method for controlled cesium adsorption and desorption. Radioactive cesium was released into the environment by the accident at the Fukushima Daiichi Nuclear Power Plant on March 11, 2011. Radioactive cesium has been incorporated into clay minerals, especially mica-based minerals, in the soil of the surrounding area [10]. Cesium is strongly adsorbed to the interlayers of inorganic lamellar silicate minerals and is not readily desorbed from the adsorption layers. Therefore, developing removal methods involving cesium desorption from soil minerals is critical.

Radioactive cesium has a slow infiltration rate into the ground; thus, it adsorbs into the surface layer of the ground [11-13]. Decontamination of cesium from the ground involves direct removal of surface soil [14]. However, cesium elution from collected radioactive waste may cause secondary contamination. Therefore, a method for inhibiting cesium desorption is necessary for final disposal of this waste. The glass hardening method is an example of a final treatment of contaminated minerals in which silicate is the main component. The effects of heat treatments on cesium adsorption and desorption characteristics onto minerals were investigated since the minerals have also the same main component of silicate.

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Cesium adsorption and desorption experiments were conducted using minerals with characteristic structures and components. Desorption of cesium from bentonite, a lamellar silicate mineral, using organic and inorganic acids has been studied. Inhibition of the ion-exchange reaction by melting of the mineral surface was investigated. The minerals were calcined before and after cesium adsorption, and the cesium adsorption and desorption of these materials were investigated. In addition, the effects of cement hardening on cesium desorption were investigated.

2. Experimental

2.1 Cesium adsorption

The cesium adsorptions of a natural zeolite (Itaya, Yamagata, Japan), synthetic zeolites (A-3, A-4, and A-5, Tosoh Co., Japan), vermiculite (Hirota Shop Ltd., Japan), bentonite (Hojun Co. Ltd., Japan), and geochemical reference samples (basalt JB-1a and soil JSO-1, AIST) were studied. The main components of Itaya zeolite are mordenite and clinoptyiolite. The synthetic zeolites used in this work were zeolites A-3, A-4, and A-5, which are potassium-, sodium-, and calcium-form zeolites with pore sizes of 3, 4, and 5 Å, respectively. Cesium aqueous solutions with concentrations of 200 and 2000 mg/L were prepared from a standard cesium chloride solution. The particle diameters of all minerals were less than 0.149 mm. Cesium adsorption equilibrium of the minerals in this study was achieved within 5 min for the zeolites and within 30 min for the other minerals. The cesium solution (50 mL) and a mineral sample (0.5 g) were placed in a 200 mL polystyrene container and stirred for 2 h. Each sample solution was filtered with a 0.20 μm syringe filter, and the amounts of adsorbed cesium were determined by measuring the cesium concentrations in the filtrates by inductively coupled plasma-mass spectrometry (ICP-MS, ELAN-DRCII, PerkinElmer Japan). The minerals were calcined in air at 400°C, 600°C, 800°C, or 1000°C. Cesium adsorption experiments for the calcined minerals were conducted using the same procedure as that used for cesium adsorption without calcination.

The crystal structures were characterized by X-ray diffraction (XRD Ultima IV, Rigaku).

2.2 Cesium desorption

Bentonite was used in the desorption experiments because it showed higher cesium adsorption ability than the vermiculite. First, pure water was used to investigate the desorption behavior. The effects of hydrochloric acid, nitric acid, sulfuric acid, oxalic acid, tartaric acid, phthalic acid, and ammonium ions on cesium desorption were also studied. Ammonium aqueous solutions with concentrations of 0.1 mol/L were prepared from ammonium chloride. The desorption solution, comprising 25 mL of 0.1 mol/L acid or ammonium solution, and 0.25 g bentonite with adsorbed cesium were placed in a 200 mL polystyrene container and stirred for 2 h. The sample solutions were filtered with a 0.20 μm syringe filter. The amounts of desorbed cesium were determined by measuring the cesium concentration in each filtrate via ICP-MS.

2.3 Cesium desorption after calcination

Minerals saturated with adsorbed cesium were obtained by the adsorption procedure described in Section 2.1; they were calcined in air at 400°C, 600°C, 800°C, or 1000°C. Cesium desorption experiments from the calcined minerals using 0.1 mol/L hydrochloric acid and ammonium oxalate solution were conducted using the procedure described in Section 2.2. The surface morphologies of the calcined minerals were determined using scanning electron microscopy (SEM; JSM-7600FA, JEOL).

2.4 Cement hardening

Ordinary Portland cement (OPC; Sumitomo Osaka Cement Co. Ltd., Japan) was used in the experiments. Cesium adsorption onto OPC itself was investigated with and without hardening. A hardened OPC sample was acquired by kneading 7.5 g OPC and 3.5 mL of pure water until fully mixed. The mixture was shaped into a block at room temperature, and then cured for one week. Finally, it was ground into powder in a mortar. Cesium solution (50 mL, 200 ppm) and 0.5 g of OPC or the hardened OPC sample were placed in a 200 mL polystyrene container and were stirred for 2 h. The sample was subjected to the procedure described in Section 2.1. The cement-hardened samples were acquired by kneading 0.5 g mineral, 6.5 g OPC, and 3.5 mL of 700 μg cesium solution until fully mixed. The mixtures were shaped into blocks at room temperature. The cement samples were cured for one week and were ground into powder in a mortar. Cesium desorption tests were performed in pure water without coexisting ions to evaluate the effects of cement hardening on cesium desorption. The cesium desorption tests were conducted as follows. Each of the samples was mixed with a pure water-to-mass ratio of 1:10 and was stirred for 6 h in a 200 mL polystyrene container. The mixtures were filtered with a 0.20 μm syringe filter, and the cesium concentrations were measured by ICP-MS.

3. Results and Discussion

3.1 Adsorption behavior of cesium on minerals

Cesium ions are adsorbed by ion exchange within the
interlayers of minerals and in the pores of zeolites. As shown in Table 1, the amount of cesium adsorbed on bentonite and the zeolites (11.3 to 104.1 mg) were greater than those adsorbed on the geochemical reference samples (1.9 to 2.6 mg) in each initial cesium concentration. Large amounts of cesium were adsorbed on bentonite and the zeolites because of their lamellar or skeleton structures and their large numbers of exchangeable cation adsorption sites. The cation-exchange capacities (CEC) of Itaya zeolite (containing clinoptilolite and mordenite) and the ideal structure of bentonite are 1.3 and 0.831 mmol/g, respectively. In contrast, CEC and the amounts of cesium adsorption were close to each other (2.6 mg). This is due to the pore sizes of the synthetic zeolites because the ionic radius of cesium is smaller than the zeolite pore size. However, the amounts of cesium adsorbed on the synthetic zeolites were lower than that adsorbed on Itaya zeolite. This low adsorption ability can be attributed to the pore sizes of the synthetic zeolites, which are too large to enable cesium adsorption. The large amounts of the exchangeable cations in pore of synthetic zeolites were eluted through ion-exchange reaction with hydrogen ion by only putting them into pure water. The pH of those aqueous solutions were about 8.9 by decreasing of hydrogen ion amounts in the water. In addition, the cesium adsorptions of the synthetic zeolites were lower than that of Itaya zeolite due to inhibition of cesium adsorption by the large amounts of potassium ion, sodium ion, and calcium ion present in the synthetic zeolites. We considered that the selective adsorptivity of cesium to this synthetic zeolite is lower than one of other cations.

Table 1  Amounts of Cs\(^{+}\) adsorbed on 0.5 g of mineral samples. The initial cesium concentrations were 200 mg/L (vermiculite, JB-1a, and JSO-1) or 2000 mg/L (bentonite, Itaya zeolites, and synthetic zeolites).

| Mineral          | Cesium adsorption amounts [mg] |
|------------------|--------------------------------|
| Itaya zeolite    | 104.1                          |
| A-3              | 11.3                           |
| A-4              | 11.4                           |
| A-5              | 11.4                           |
| Bentonite        | 71.3                           |
| Vermiculite      | 2.7                            |
| JB-1a            | 2.6                            |
| JSO-1            | 1.9                            |

Zeolites are used as adsorbents and catalysts owing to their high adsorption capacities for cations through ion-exchange reactions. Generally, natural zeolite is formed by compression and heating of volcanic ash caused by ground pressure and heat from lava. Itaya zeolite adsorbed the most cesium because of the high CEC values of its mordenite and clinoptilolite contents. Cesium ions readily enter the pores of the synthetic zeolites because the ionic radius of cesium is smaller than that of the zeolite pore size. However, the amounts of cesium adsorbed on the synthetic zeolites were lower than that adsorbed on Itaya zeolite. This low adsorption ability can be attributed to the pore sizes of the synthetic zeolites, which are too large to enable cesium adsorption. The large amounts of the exchangeable cations in pore of synthetic zeolites were eluted through ion-exchange reaction with hydrogen ion by only putting them into pure water. The pH of those aqueous solutions were about 8.9 by decreasing of hydrogen ion amounts in the water. In addition, the cesium adsorptions of the synthetic zeolites were lower than that of Itaya zeolite due to inhibition of cesium adsorption by the large amounts of potassium ion, sodium ion, and calcium ion present in the synthetic zeolites. We considered that the selective adsorptivity of cesium to this synthetic zeolite is lower than one of other cations.

The cesium adsorption amounts for the reference samples, JB-1a and JSO-1, were lower than those for the zeolites and bentonite. This is due to the uneven skeleton structures of JB-1a and JSO-1. Based on the component data from AIST, the contents of elements that affect ion exchange (sodium, magnesium, potassium, and calcium) of JB-1a and JSO-1 are 21.27% and 9.97%, respectively. Although the number of exchangeable cations in JB-1a was twice that in JSO-1, the amounts of cesium adsorption were close to each other (2.6 and 1.9 mg). This is due to the surface hydroxyl groups of the corrosion product on JSO-1. Cesium ion was also adsorbed on these surface hydroxyl groups.

As shown in Table 2, the amounts of cesium adsorbed on the calcined minerals decreased with increasing calcination temperature under all experimental conditions. The number of adsorption sites decreased due to structural changes and the combustion of organic substances during calcination. Fig. 1 shows the XRD patterns of Itaya zeolite at various calcination temperatures. Patterns were observed corresponding to the components of the zeolite, namely clinoptilolite and mordenite. The clinoptilolite and mordenite patterns decreased as the calcination temperature increased.
similar to that of cesium ion. This is the probable reason for
the high desorption ratio of cesium with ammonium ion
(21–25).
Equation (1) shows the equilibrium between cesium adsorp-
tion and desorption on minerals by external cations such as
hydrogen ion and ammonium ion.
\[
\text{Cs}^+_{\text{mineral}} + \text{other cations} \rightleftharpoons \text{Cs}^+ + \text{other cations}_{\text{mineral}} \tag{1}
\]
When large amounts of cations were present in solution, the
equilibrium shifted to the right.
The ratios of cesium desorption from the natural and
synthetic zeolites with 0.1 mol/L hydrochloric acid were 5.4%
and 70% to 75%, respectively. The amounts of aluminum ion
eluted from 5 g of Itaya zeolite and synthetic zeolite A-3 by
100 mL of 0.01 mol/L hydrochloric acid were 64 and 1742 mg/
L, respectively. The amount of aluminum eluted from the
synthetic zeolite was higher than that eluted from Itaya zeo-
lite. The high desorption ratio of cesium from the synthetic
zeolite may be attributed to its framework, which contains
aluminum, silicon, and oxygen; this framework is more read-
ily degraded by hydrochloric acid than that of Itaya zeolite.

3.3 Cesium desorption after calcination
The cesium desorption ratios of the geochemical reference
samples were high due to the weak interactions between
the minerals and cesium ion. However, the desorption
ratios decreased owing to the calcination of the minerals;
the desorption amount of cesium adsorbed by the minerals
decreased as the calcination temperature increased (Table 4).
Like the cesium desorption ratios for JB-1a and JSO-1, those
for Itaya zeolite, bentonite, and vermiculite became a mini-
mum value at 1000°C.

Fig. 2 shows SEM images of Itaya zeolite surface after
calcination at different temperatures. After calcination at
1000°C, the surface of the zeolite was smooth, indicating
the occurrence of melting and re-solidification (Fig. 2(d)).
Therefore, calcination caused changes in the soil interlayer and pore structures, melting of minerals, and trapping of exchangeable cations at the ion-exchange sites. In addition, the XRD patterns of JB-1a and JSO-1 were confirmed to contain patterns for $\text{Cs}_4\text{Al}_4\text{Si}_{20}\text{O}_{48}$ trapping cesium in the crystal (Fig. 3). The possibility of cesium volatilizing from the mineral surface was considered; however, cesium adsorbed within the minerals did not volatilize because small amounts of cesium were desorbed from the calcined minerals. Actually, small amounts of cesium were eluted from the calcined minerals at 1000°C with 0.1 mol/L hydrochloric acid because the mineral surface was dissolved by the acid.

### Table 4  Desorption ratios (%) of cesium at various calcination temperatures to the cesium adsorption amounts of the respective uncalcinated minerals in Table 1.

|                     | Water 400°C | Water 600°C | Water 800°C | Water 1000°C | Hydrochloric acid (pH 1) 400°C | Hydrochloric acid (pH 1) 600°C | Hydrochloric acid (pH 1) 800°C | Hydrochloric acid (pH 1) 1000°C | Ammonium ion (pH 6.5~7.0) 400°C | Ammonium ion (pH 6.5~7.0) 600°C | Ammonium ion (pH 6.5~7.0) 800°C | Ammonium ion (pH 6.5~7.0) 1000°C |
|---------------------|-------------|-------------|-------------|-------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| Itaya zeolite       | 0.3         | 0.2         | 0.2         | 0.2         | 3.2                           | 4.2                           | 6.8                           | 0.2                           | 5.1                           | 6.0                           | 9.2                           | 0.2                           |
| Bentonite           | 0.7         | 0.6         | 0.3         | 0.4         | 22.6                          | 23.2                          | 17.2                          | 0.5                           | 20.5                          | 23.4                          | 18.1                          | 0.3                           |
| Vermiculite         | 4.7         | 1.9         | 2.4         | 0.4         | 34.5                          | 9.4                           | 2.7                           | 1.1                           | 11.5                          | 3.5                           | 1.2                           | 0.4                           |
| JB-1a               | 3.4         | 2.2         | 0.6         | 0.2         | 87.1                          | 47.1                          | 4.8                           | 1.4                           | 52.5                          | 24.6                          | 1.5                           | 0.7                           |
| JSO-1               | 11.2        | 13.0        | 5.9         | 0.5         | 88.6                          | 50.2                          | 23.8                          | 2.6                           | 36.5                          | 26.6                          | 7.4                           | 0.6                           |

Fig. 2  SEM images of Itaya zeolite (a) without calcination and after calcination at (b) 600°C, (c) 800°C, and (d) 1000°C. Magnification: 10,000×.

3.4 Desorption of cesium from cement

The unhardened OPC did not adsorb cesium ions, whereas 0.5 g of the hardened cement adsorbed 234 μg of cesium. The cesium adsorption rates on the minerals were much faster than on cement. Therefore, we considered that the cement mixtures hardened after cesium was adsorbed onto the minerals during simultaneous addition and kneading of the mineral and cement. Cesium desorption from the cement samples containing cesium-loaded minerals was inhibited by cement hardening (Table 5). This is probably because the cement hydrates that coated the mineral particle surfaces have cesium adsorption abilities. However, small amounts
Table 5  Effects of cement hardening on the ratios of cesium desorption (%) from minerals into water to the addition amount of cesium: 700 μg.

| Mineral      | Without cement hardening | Cement hardening |
|--------------|--------------------------|------------------|
| Cement only  | < LOQ*                   | 0.2              |
| Itaya zeolite| 0.7                      | < LOQ*           |
| Bentonite    | 0.9                      | 0.3              |
| Vermiculite  | 15.6                     | 0.8              |
| JB-1a        | 31.0                     | 1.3              |
| JSO-1        | 39.2                     | 1.4              |

LOQ*: limit of quantification

Fig. 3  XRD patterns of (a) JB-1a and (b) JSO-1 after calcination at 1000°C.

4. Conclusions

Bentonite adsorbs large amounts of cesium because inorganic lamellar silicates swell readily and contain large amounts of exchangeable cations. The cesium adsorption of Itaya zeolite is affected by its high CEC value and the mordenite and clinoptilolite in its skeleton structure. The amount of cesium adsorbed on A-type zeolites is low owing to the large pore size of the synthetic zeolites and their high cation content. Cesium adsorption on the geochemical reference samples was related to the amounts of exchangeable cations and surface hydroxyl groups of the corrosion products. The combination of acid and ammonium ions promoted desorption of cesium. Hydrochloric acid dissolved large amounts of aluminum ions from the skeleton structure of a synthetic zeolite. The amounts of cesium adsorbed on and desorbed from all minerals decreased as the calcination temperature increased. Thus, calcination may trap cesium in the ion-exchange sites of minerals. Cesium desorption from cement samples containing cesium-loaded minerals was inhibited by coating the minerals with cement hydrate and by subsequent adsorption of cesium onto the cement hydrate.

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