Mechanism of Cs Removal from Fukushima Weathered Biotite by Heat Treatment with a NaCl–CaCl₂ Mixed Salt

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ABSTRACT: An in situ extended X-ray absorption fine structure (in situ EXAFS) spectroscopic analysis at high temperature was conducted to investigate the mechanism of Cs removal from weathered biotite (WB) from Fukushima, induced by heating with a mixed salt of NaCl and CaCl₂. This indicated that most Cs remained in WB during heating at 200−700 °C. In addition, the in situ EXAFS spectra gradually changed on heating with the mixed salt and a completely different spectrum was observed for the sample after cooling from 700 °C to room temperature (RT). Ex situ EXAFS measurements and X-ray fluorescence analyses were also conducted on samples after heat treatment and removal of the mixed salt to clarify the temperature dependence of the Cs removal ratio. On the basis of the results of radial structure function analysis obtained from in situ EXAFS, we concluded that almost all of the Cs was removed from WB by heating at 700 °C with the mixed salt, and that Cs formed Cs−Cl bonds after cooling to RT from 700 °C. In contrast, although more than half of the Cs present was removed from WB by heat treatment at 500 °C, most Cs was surrounded by silica tetrahedrons, maintained by Cs−O bonds. On the basis of these results, different Cs removal processes are suggested for the high-temperature (600−700 °C) and low-temperature (400−500 °C) regions.

INTRODUCTION

Following the accident at the Fukushima Daiichi Nuclear Power Plant on March 11, 2011, many fission products, including ¹³⁴Cs and ¹³⁷Cs, were released into the air and distributed over a wide area around the northern Kanto and Tohoku regions (especially Fukushima) of Japan; soil contamination by radioactive materials is still a significant problem.¹−³ ¹³⁷Cs represents a particularly significant hazard because this isotope has a half-life of approximately 30 years and strongly adheres to soil particles, especially clay minerals. Consequently, ¹³⁷Cs contamination is primarily observed within the upper 5 cm of affected soils;⁴ huge amounts of contaminated soils were gathered and accumulated at many temporary storage sites. Although volume reduction of the contaminated soil is an important social problem, a standard Cs removal method has not been established for soil.

In Fukushima, as is well known, Cs is selectively and strongly sorbed in a specific clay mineral known as weathered biotite (WB), which forms a significant fraction of soils.⁵−⁹ WB, one of the most common clay minerals in the soil in Fukushima, occurs as a mixed layer structure comprising biotite from the Abukuma granite and vermiculite formed by weathering.¹⁰ Recent studies have shown that compared with biotite, illite, smectite, kaolinite, halloysite, allophane, and imogolite Cs is more selectively sorbed in WB in Fukushima soil.¹¹ Therefore, WB is one of the most important topics in research on Cs sorption in Fukushima.

A method for the sublimation of Cs using heat treatment was previously examined¹² for the removal of Cs from clay minerals, such as WB and soil. Normal heat treatment up to 1300 °C fixes Cs onto silicate to form a stable silicate mineral without any radioactivity loss; however, heat treatment with certain types of alkali salts enhances Cs removal.¹³ Spalding reported a reduction of more than 99% in radioactivity by adding NaCl and limestone to Cs-contaminated soil and heating it to a temperature above 1000 °C.¹⁴ Shimoyama et al. added NaCl and CaCl₂ (NaCl–CaCl₂) mixed salts to Cs-sorbed WB, conducted heat treatment in a low-pressure environment at 650 °C accompanied by aqueous cleaning of the sample, and then performed X-ray photoelectron spectroscopy analysis. They reported that the Cs 3d peak corresponding to nonradioactive Cs almost disappeared.¹⁵ The results of these previous studies demonstrated the effectiveness of heat treatment with alkali salts in the removal of Cs from WB.

Although the above-mentioned high-temperature heat treatments are effective Cs removal methods, their high cost is problematic; thus, it is desirable to keep the treatment
We also conducted ex situ EXAFS measurement and X-ray fluorescence (XRF) spectroscopic analysis on samples from which the alkali salt had been removed after heat treatment to determine the temperature dependence of the Cs removal ratio. Finally, on the basis of the obtained Cs removal ratio and the results of in situ EXAFS in this study, we concluded that different Cs desorption processes occur in the temperature ranges of 400–500 and 600–700 °C.

RESULTS AND DISCUSSION

We first compared the pure WB sample with that containing both WB and the NaCl–CaCl₂ mixed salt using Cs K edge EXAFS measurements. The red and black curves in Figure 1, respectively, show the Cs K edge EXAFS spectra of the WB sample (A) and the WB–NaCl–CaCl₂ mixed salt sample (B) before heating. The two spectra have similar shapes at the peaks labeled a, b, and c. This means that the Cs in WB is not influenced by the addition of the mixed salt at room temperature (RT).

We then investigated the effect of the NaCl–CaCl₂ mixed salt addition on the EXAFS spectra at high temperatures. Figure 2a,b shows EXAFS spectra of samples (A) and (B) at high temperatures, respectively: the black, lilac, blue, pink, purple, indigo, and red curves correspond to the results for temperatures of 200, 300, 400, 500, 600, and 700 °C, respectively. The green curves represent the EXAFS spectra obtained after cooling to RT from 700 °C. The insets show three typical spectra: at RT, on heating to 700 °C, and after cooling.

The WB sample spectral shapes were almost the same in all cases (Figure 2a). Indeed, the spectra showed only slight differences, as observed in the insets of Figure 2. This result indicates that, as the temperature increased, the amplitude of the fine structure gradually decreased. As temperature increases, atomic vibrations have larger amplitudes and the Debye–Waller factor is proportional to temperature. Therefore, we consider that the local structure of Cs did not change under these conditions; in fact, after cooling, the spectrum returned to its original shape, that is, that before heating.

In contrast, for the case of the sample of WB and NaCl–CaCl₂ mixed salt (Figure 2b inset), the spectra at RT, 700 °C, and after cooling show that an irreversible change occurred. With the NaCl–CaCl₂ mixed salt, the heating contribution is much more evident, and the fine structures at the edge exhibit much broader features as the temperature reaches 700 °C. After cooling, the spectrum did not return to its original shape. This result indicates that the local structure of Cs in WB was changed by heat treatment with the NaCl–CaCl₂ mixed salt.

We therefore performed EXAFS analysis of the Cs K edge spectra to understand the local structure around Cs in both samples. EXAFS analysis was successfully conducted in the past to reveal the local structure of Cs-sorbed WB. The EXAFS data were analyzed here using WinXAS ver. 3.2 developed by Ressler and FEFF 8.40 developed by Zabinsky. The k³-weighted χ(k) spectra of Cs K edge EXAFS for samples (A) and (B) are shown in Figure 3a,b, respectively.

The χ(k) function weighed by k³ was Fourier transformed to obtain an RSF with a k-range of less than 8 Å⁻¹. This k-range was chosen because the influence of noise was more significant above 8 Å⁻¹ in the case of sample (B). Structural parameters, such as the intrinsic distance, the coordination number, and the Debye–Waller factor, were obtained by least-squares fittings in the k-space. In this report, we focused on changes in the bond pairs and positions; these parameters were only used for identification of these factors.

For the case of sample (A), the amplitude of the EXAFS function was proportional to temperature, but the vibration period was similar for all temperatures. The spectrum returned to its original shape after cooling from a high temperature to RT. This suggests that most Cs remained in the silicate when WB was heated to 700 °C in air without the alkaline salt. In sample (B), the amplitude of the EXAFS function was almost the same up to 400 °C; however, above 500 °C, it became smaller. Furthermore, the spectral shape changed significantly after cooling from 700 °C to RT, indicating that the heat treatment changed the local structure around Cs.

Two main peaks are observed at 2.0 and 3.4 Å before heating (Figure 3c). Regarding the local structure of Cs in WB, it is suggested that Cs⁺ ions are strongly sorbed at the siloxane ditrigonal cavity (SDC) sites in micaceous clay minerals, such as clay minerals, in multicomponent systems conducted. Using EXAFS, it is possible to observe particular phases, such as clay minerals, in multicomponent systems using the element selectivity arising from inner-shell excitation. This method is advantageous for obtaining information on local structural changes involving Cs, which is not possible via methods that identify changes in the crystal structure, for example, X-ray diffraction analysis. To investigate the effect of molten alkali salts on clay minerals, we added a NaCl–CaCl₂ mixed salt to the studied samples, conducted in situ EXAFS measurements at 200–700 °C, and then compared the differences in the spectra with and without the alkali salt. We also conducted ex situ EXAFS measurement and X-ray fluorescence (XRF) spectroscopic analysis on samples from which the alkali salt had been removed after heat treatment to determine the temperature dependence of the Cs removal ratio.

Finally, on the basis of the obtained Cs removal ratio and the results of in situ EXAFS in this study, we concluded that different Cs desorption processes occur in the temperature ranges of 400–500 and 600–700 °C.

Figure 1. Cs K edge EXAFS spectra for (A) WB + NaCl–CaCl₂ at RT and (B) only WB at RT before heating.
as WB. On the basis of the adsorption model at the SDC site, the peak at 2.0 Å is attributed to Cs−O pairs, and the peak at 3.4 Å is attributed to Cs−Si pairs. The Cs−O peak appeared at almost the same position from 200 to 700 °C, and we observed a small increase in distance after cooling. Although the origin of the peak shift is not clear, we consider that most Cs remained at the SDC sites because the Cs−Si peak was observed at almost the same distance before and after heat treatment. Therefore, we infer that Cs was not removed from WB after heat treatment with the NaCl CaCl2 mixed salt. Therefore, a coordination structural change around Cs was indicated. We cannot, however, estimate how much Cs was removed from WB after heat treatment with the NaCl CaCl2 mixed salt because in situ EXAFS analysis gives only average information for all Cs atoms.

In contrast, we observed a different tendency of the RSF for sample (B). Focusing only on the first peak at the bottom of Figure 3d, the addition of the NaCl−CaCl2 mixed salt induced a shift toward the higher distance end at 500 °C. This means that the local structure around Cs was modified by the influence of the salt at high temperatures. In the 500 °C spectrum, the shift of the first peak corresponded to a change in interaction between the Cs+ ions and the silica layers in WB. As the temperature approached 700 °C, we observed that the bond length of the first peak increased. This implies that a portion of Cs desorbed from WB and was eluted in the NaCl−CaCl2 mixed salt. Therefore, a coordination structural change around Cs was indicated. We cannot, however, estimate how much Cs was removed from WB after heat treatment with the NaCl−CaCl2 mixed salt because in situ EXAFS analysis gives only average information for all Cs atoms.

We therefore estimated the Cs removal ratio using ex situ EXAFS and XRF measurements. Figure 4a shows the ex situ EXAFS spectra at the Cs K edge after removing the salt by water rinsing; the black, red, blue, pink, and green curves correspond to the results before heating and after heating at 400, 500, 600, and 700 °C, respectively. A strong edge jump was observed before heating, and its intensity decreased with heating temperature because eluted Cs in the NaCl−CaCl2 mixed salt was rinsed away with water. In fact, no edge jump was observed for heating at 700 °C. This result suggests that 99.8% (almost 100%) Cs was removed from WB after heat treatment with the mixed salt.

In Figure 4b, the black squares represent the relative intensities of the Cs edge jump obtained from the ex situ EXAFS measurements as a function of the heating temperature. Here, the edge jump data for particular temperatures are normalized to a value of unity for the sample before heating. The shaded bars show the relative amounts of Cs remaining in the sample obtained from XRF measurements as a percentage of the amount of Cs present before heating. XRF analysis clarified that the amount of Cs in the sample decreased by 56, 61, 89, and 100% at 400, 500, 600, and 700 °C, respectively. As shown in Figure 4b, both ex situ EXAFS and XRF values showed similar tendencies. This indicates that the in situ EXAFS spectrum of sample (A) after cooling originated from Cs eluted in the NaCl−CaCl2 mixed salt; the first peak in the RSF of Figure 3d is therefore attributed to the presence of Cs−Cl bonds.

Here, we discuss the Cs removal process by comparing the Cs removal ratio based on the in situ EXAFS analyses. As previously noted, these results for sample (B) indicated that Cs was removed from WB with the salt at 400 °C; however, as already inferred from XRF analysis, 56% of the Cs was removed from the WB with the salt at 400 °C after washing the sample with water. Consequently, the in situ EXAFS spectrum obtained at 400 °C contained both Cs remaining in WB and eluted in the NaCl−CaCl2 mixed salt; however, Cs in WB is maintained in a Cs−O structure in the 400 °C heating process.

In contrast, in situ EXAFS clarified that the bond length of the first peak in RSF gradually increased above 500 °C, and XRF analysis showed that the Cs removal ratio increased as this peak shifted to the longer side. The layered silicate structure in WB was thus gradually dissolved by the influence of the NaCl−CaCl2 mixed salt, and the ratio of Cs−Cl bonds to Cs−O bonds increased with temperature.

This interpretation means that both Cs−O and Cs−Cl bonds contributed to the first peak in the RSF of Figure 3d; therefore,
it is important to distinguish these in the RSF. A previous EXAFS analysis reported that the Cs–Cl bond length was 2.9 Å at RT and 2.4 Å at 700 °C. In EXAFS analysis, it is known that the distance shortens as the temperature increases. Furthermore, the 2.9 Å position seems closer to that of hydrated cesium (Cs–O), but the electron density around the scattering Cs atoms is quite different when comparing Cl with O: in this case, the electron density of Cl is higher than that of O. In addition, a comparison of standard samples with CsCl and NaCl–CaCl₂ mixed salts was conducted, which confirmed that the 2.9 Å position agreed with that of the Cs–Cl distance. This bond shortening at 700 °C resulted from a phase transition from the crystal to the molten salt form because the melting point of CsCl is approximately 645 °C. Hence, it is hypothesized that the Cs–Cl bond length would shift from 2.9 to 2.4 Å with increasing temperature and that the bond length would be close to 2.9 Å below the melting point. We consider that the first peak at 400 °C in the RSF of Figure 3d should not be attributed to the Cs–Cl bond, but to the Cs–O bond, for two reasons: the first is that the eutectic point of the NaCl–CaCl₂ mixed salt was confirmed using differential thermal analysis to be 504 °C, which is higher than 400 °C; the second reason is that the bond length for the first peak (2.0 Å) is much shorter than the Cs–Cl bond length in the solid state (2.9 Å). Therefore, if half of the Cs present was eluted in the mixed salt at 400 °C, we would observe a Cs–Cl peak around 2.9 Å. We assume that the same would also be partially true at 500 °C because the bond length of the first peak was 2.1 Å at 500 °C in the RSF of Figure 3d; however, we consider that a portion of the Cs may be eluted in the NaCl–CaCl₂ mixed salt above 600 °C because the bond length increased to 2.4 Å at 600 and 700 °C.

Figure 3. Cs K edge EXAFS spectra for Cs-sorbed samples. (a, b) k³-weighted χ(k) spectra for samples (A) and (B), respectively. (c, d) Corresponding radial structure functions (RSFs) obtained from (a) and (b), respectively.
Considering all of the above, we propose the existence of at least two Cs removal processes: a process dominant in the high-temperature region above 600 °C and another dominant in the low-temperature region below 500 °C.

In the high-temperature process, Cs is released and eluted in the mixed salt through the heating process. We think that the ratio of the extents of the high-temperature to the low-temperature process gradually increases with temperature because the first peak in RSF approaches the Cs–Cl bond length at higher temperatures, as observed in Figure 3d.

In the low-temperature process, we suggest a hypothesis that Cs is surrounded by silica tetrahedrons during heating but is released from the silicate structure through the cooling process. This implies that some change in the layered silicate structure occurs during the cooling process in the presence of the alkaline salt. In fact, water molecules formed during the dehydroxylation of biotite might temporarily increase its d-spacing, which would accelerate the cation-exchange reactions between interlayer Cs, Na, and Ca. With regard to the process by which Cs is removed from WB, we investigated the influence of water washing without heat treatment to avoid possible incorrect interpretation of Cs removal results. To confirm this, a well-stirred sample of WB with the mixed salts was washed with water and then subjected to XRF analysis. This showed that there was no change in the Cs remaining in the sample, which indicated that the washing step by itself did not influence the Cs removal process. It is not a coincidence that the observation of a change in Cs coordination occurred at temperatures of 500–700 °C.

These insights may be helpful in improving our method of Cs decontamination from soil. We will investigate the low- and high-temperature processes in more detail by measuring in situ EXAFS, not only for the heating process but also for the cooling process, in future work. If the low-temperature process dominates at 500 °C, we can expect some hysteresis of the in situ EXAFS spectra between the heating process up to 500 °C and the cooling process above 500 °C. Furthermore, we plan to study the role of alkaline salts in future work. If the hysteresis of the in situ EXAFS spectra depends on the presence of alkaline salts, this information would give us important clues with respect to choosing particular alkaline salts as reagents for Cs decontamination.

In our present study, we investigated the local structure of Cs sorbed in WB using in situ and ex situ EXAFS measurements at the Cs K edge to study the Cs removal process from this clay mineral by heating from 200 to 700 °C. The results of in situ EXAFS clarified that most of the Cs remained in WB during the heating. In contrast, we observed that the in situ EXAFS spectra gradually changed on heating with a NaCl–CaCl₂ mixed salt; a completely different spectrum was observed for the sample after cooling from 700 °C to RT. Ex situ EXAFS spectra were measured for Cs-sorbed WB after heat treatment with the NaCl–CaCl₂ mixed salt and rinsing the salt from the sample with water; the edge jump of the ex situ EXAFS spectra decreased with temperature, indicating increasing Cs removal from WB and its elution in the NaCl–CaCl₂ mixed salt. Cs removal ratios were estimated for the samples based on XRF measurements; they exhibited a similar tendency to that of the decrease in the edge jump of ex situ EXAFS spectra. On the basis of the Cs removal ratios and the RSF analysis obtained from in situ EXAFS with the salt, we conclude that almost all Cs can be removed from WB by heat treatment at 700 °C; RSF indicated the formation of Cs–Cl bonds after cooling from 700 °C to RT. In contrast, despite the fact that more than half of the Cs was removed from WB by heat treatments at 400 and 500 °C, RSF shows that most Cs is surrounded by silica tetrahedrons maintained by Cs–O bonds. We therefore confirmed the Cs removal process in the high-temperature region: Cs is released from the clay minerals during heating in the high-temperature process. In contrast, Cs removal in the low-temperature region cannot be explained in the same manner, and we therefore presume that another Cs removal process exists under these conditions. In this work, we succeeded in demonstrating the usefulness of in situ EXAFS analysis for the study of Cs removal from a clay mineral. This new knowledge allows us to establish a method for Cs decontamination from soil in Fukushima.

**MATERIALS AND METHODS**

A WB sample, which originated from the weathering of local granite, was collected from Fukushima. This WB has been completely characterized by Kikuchi et al. Cs sorption experiments were performed according to a well-known method. The Cs-sorbed samples were prepared as follows: the clay minerals were dispersed into a 1.0 × 10⁻¹ mol L⁻¹...
CsCl solution for 24 h while slowly stirring; the solution was then centrifuged to separate the solid and the liquid, and the supernatant was discarded. The $1.0 \times 10^{-1}$ mol L$^{-1}$ CsCl solution was added again, and the above procedure was repeated five times. The remaining clay mineral was then washed with distilled water and the presence of negligible CsCl was confirmed by adding a silver nitrate solution and verifying that the suspension was free of white turbidity. The sample was then dried by a freeze-drying machine. WB was ground and washed with distilled water and the presence of negligible CsCl anticipated a small absorption loss due to the high X-ray absorption coefficient.

We used the electronic furnace developed by Okamoto et al. for in situ EXAFS measurements at high temperatures. In situ EXAFS spectra were measured every 100 °C from 200 to 700 °C, maintaining a constant temperature during the measurements. We also measured EXAFS spectra at RT after heating. Cs K edge EXAFS spectra were measured using the BL11XU beamline in SPring-8. We adopted the K edge because we had a diameter of 10 mm and a thickness of 1 mm. The quartz cell for the in situ EXAFS measurements with a light path length of 1 mm between two pieces of the quartz board, which had a diameter of 10 mm and a thickness of 1 mm. Approximately 100 mg powder sample was loaded in the quartz cell. The X-ray energy at the Cs K edge was calibrated to 35.98 keV using a 0.1 mol L$^{-1}$ CsCl solution. The EXAFS data analysis, including background removal, normalization, extraction of the EXAFS function, and Fourier transformation, was performed using WinXAS version 3.2.

In addition, we measured ex situ EXAFS spectra at RT for samples after heat treatment and removal of the salt to estimate the amount of residual Cs in the sample. Ex situ EXAFS measurements at the Cs K edge were also performed using the BL11XU beamline and quartz cell. We conducted quantitative analysis of residual Cs in WB based on the edge jump intensity in each EXAFS spectrum, which was defined as the intensity ratio of the peak at 35.98 keV before and after subtraction of the background curves using the Athena software.

We prepared samples for ex situ EXAFS measurements as follows: the heat treatment was performed using an electric furnace (KTF045N1; KOYO Thermo Co., Ltd.); NaCl–CaCl$_2$ mixed salt addition was as described above. Samples were heated at a constant rate of 15 °C/min in air, and the temperature was maintained constant for 120 min at each measurement level (200, 300, 400, 500, 600, and 700 °C). After heating, the samples were mixed with 10 mL distilled water, the solution was centrifuged to separate the solid from the liquid, and the supernatant was discarded. The samples were then freeze-dried. To estimate the Cs content after washing of the salt from the sample, the dried residues were analyzed by scanning wavelength-dispersive XRF spectroscopy (Rigaku; ZSX Primus II). Wavelength-dispersive XRF has higher resolution than energy-dispersive XRF. In addition, mapping measurement is possible on a sample image. The Cs content of the original WB specimen was estimated at approximately 1 mass % as a standard sample.

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