Proposed Cesium-free Mineralization Method for Soil Decontamination: Demonstration of Cesium Removal from Weathered Biotite

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ABSTRACT: The removal possibility of sorbed Cs from weathered biotite (WB), which is considered a major Cs adsorbent in the soil of Fukushima, has been investigated by the addition of an NaCl−CaCl2 mixed salt powder with a 1:1 ratio of Na and Ca and subsequent heat treatment under a reduced pressure of 14 Pa. X-ray fluorescence analysis was used to determine the Cs removal rate at elevated temperatures. The structural changes and new phases formed were determined using powder X-ray diffraction as well as electron diffraction and X-ray microanalysis in a transmission electron microscope. We found that Cs was completely removed from the specimen heated at 700 °C, where WB completely decomposed and augite was formed. On the basis of this finding, we propose the Cs-free mineralization method as a new soil-decontamination process in which Cs minerals are transformed by heating with certain additives into minerals that cannot incorporate Cs.

INTRODUCTION

A large quantity of radioactive nuclides was scattered by the Fukushima Daiichi Nuclear Power Plant accident that occurred in March 2011. Most of them were deposited on the soil around Fukushima prefecture, and more than 20 million m³ of radioactive contaminated soil was placed in temporary storage facilities as a result of the decontamination process of the land. This soil is to be managed in middle storage facilities for the next 30 years. Therefore, volume reduction of the contaminated soil is an emergent problem. Among the scattered radioactive nuclides, 137Cs is the major source of radiation because of its large quantity and relatively long half-life. Most of the 137Cs has been reported to be strongly fixed to clay minerals, especially weathered biotite (WB), in the soil. WB is derived from granite and has a structure with interstratifications of biotite and vermiculite (or hydrated) layers formed by weathering. Such WB is ubiquitous in the soil in the eastern region of Fukushima prefecture. Removing Cs absorbed by WB using, for example, an ion-exchange process with other cations is difficult, although the efficient removal of Cs from soil by hydrothermal treatment with MgO has been reported.

Heat treatment is a highly efficient soil-decontamination treatment. The basic concept of the treatment involves heating with the addition of an alkali chloride to the soil. As a result, clay minerals in the soil melt and Cs sorbed to the minerals sublimates as a chloride. According to a previous report, more than 99% of Cs can be removed using this method. However, heating to temperatures greater than 1000 °C is necessary to melt clay minerals, which leads to a high cost of this process. By contrast, we have developed a new process to remove most Cs from WB. This process involves adding a mixed salt to WB and heating the mixture to 650 °C under a reduced pressure of 14 Pa; thereafter, the mixture is washed with water to remove Cs effectively. In addition, we have clarified that the chemical bonding of Cs changes from Cs−O bonding to Cs−Cl bonding upon heat treatment at 700 °C. Thus, Cs can be eluted into the salt from WB and subsequently removed at low temperatures by washing away the excess salt. Because Cs is washed away, we need to consider its effect on the surrounding physical environment.

In this study, we have investigated the Cs removal rate and structural changes in WB resulting from heat treatment in the...
presence of added NaCl–CaCl₂ mixed salt. We analyzed the removal rate and the structural change by X-ray fluorescence (XRF) analysis and X-ray diffraction (XRD) analysis, respectively. In addition, the characteristics of the crystal structure before and after the treatment were examined by transmission electron microscopy (TEM). As a result, new crystal phases were observed to emerge at approximately 500 °C, and Cs was completely removed at 700 °C, where WB decomposed completely and a pyroxene (augite) was formed. On the basis of the results, we propose our method of Cs-free mineralization (CFM) as a new soil-decontamination process.

## RESULT AND DISCUSSION

The Cs/Si molar ratio obtained by the XRF analysis is shown in Figure 1. The Cs removal rate at 400, 500, 600, and 700 °C was 45, 47, 82, and 100%, respectively.

![Graph showing Cs/Si molar ratio at each heating temperature (no heating, 400, 500, 600, and 700 °C)](image)

**Figure 1.** Cs/Si molar ratio at each heating temperature (no heating, 400, 500, 600, and 700 °C) determined by the XRF analysis.

The XRD pattern of the specimen heated at each temperature is shown in Figure 2a. The pattern of the specimen heated at 400 °C was almost identical to that of the specimen before heating, i.e., the Cs-sorbed WB. By contrast, several new peaks, including those at 2θ = 29.4°, were observed in the pattern of the specimen heat-treated at 500 °C. Additional new peaks, including those at 33.2°, appeared after the heat treatment at 600 °C. Furthermore, the peak at approximately 8° disappeared after the heat treatment at 700 °C. Because this peak is the basal reflection of WB, its disappearance indicates that the WB was completely decomposed.

These new crystalline phases were successfully identified using the TEM analysis (Figure 2b). The peaks that appeared in the patterns of specimens treated at 500 and 600 °C are attributed to calcite (CaCO₃) and hematite (Fe₂O₃), respectively. As previously mentioned, the peaks of WB disappeared completely and a number of intense new peaks appeared. The TEM analysis revealed numerous fine crystals, as shown in Figure 2c. The energy-dispersive X-ray spectroscopy (EDS) analysis in conjunction with the TEM observations indicated a composition with Mg, Al, Si, Ca, and Fe as the major cations. The SAED patterns obtained from the crystals were reproduced using the cell parameters and space group of a clinopyroxene such as diopside (CaMgSi₂O₆), as shown in Figure 2d,e. Hence, the crystals should be termed augite, (Ca₉Na)(Mg,Fe,Al)(Si,Al)₂O₆. Most of the major peaks in the XRD pattern of the specimen treated at 700 °C were also reproduced on the basis of this mineral (Figure 2b). The TEM analysis also revealed crystals containing Cl as well as Ca, Mg, Al, Si, and Fe, whose SAED patterns are not attributable to augite. Moreover, unidentified peaks existed in the XRD pattern of the specimen treated at 700 °C. These peaks are explained by wadalite, a Ca- and CI-bearing silicate with a nominal formula (Ca₉Mg₅)(Al₁₄Si₂O₆)Cl₄. Although quantitative analysis was not performed, augite was clearly the most abundant phase in the specimen heated at 700 °C.

The crystal structure of augite viewed perpendicular to the (100) plane is shown in Figure 3a. Augite is a clinopyroxene, or single-chain inosilicate mineral, in which the M₁ site is coordinated by six oxygens, forming a regular octahedron, and the M₂ site is coordinated by eight oxygens between the single chains of silicon or aluminum tetrahedra (T sites). Larger cations such as Fe²⁺, Ca²⁺, or Na⁺ occupy M₂ sites, whereas smaller ones such as Al³⁺, Fe³⁺, or Mg²⁺ occupy M₁ sites. In general, a K⁺ ion does not easily enter an M₂ site because its ionic radius is too large to be accommodated (Figure 3b). Hence, the incorporation of K⁺ into augite has not been reported. Because the ionic radius of Cs⁺ is greater than that of K⁺ (Figure 3b), Cs⁺ is reasonably assumed to seldom enter the pyroxene structure, even in trace amount (Figure 3b). This situation is also similar to that of other mineral phases (wadalite, hematite, and calcite) formed by the heat treatment. Hence, Cs⁺ originally incorporated into WB could not find a host mineral phase and vaporized or was incorporated into the remaining salt and subsequently washed away.

With regard to the process by which Cs is removed from WB, the formation of other mineral phases (anorthite (CaAl₂Si₂O₈) and Ca₂SiO₄Cl₂ not determined by mineral analysis) was confirmed using XRD and TEM analyses. The aforementioned results suggest that radioactive Cs can be removed from contaminated soil via the phase transition of clay minerals into different silicate minerals upon heat treatment in the presence of additives. We propose this concept of cesium-free mineralization (CFM) as a new decontamination process on the basis of these findings. This process works at a considerably lower temperature than the fusion of clay minerals, which generally requires temperatures greater than 1000 °C. In addition, with judicious selection of the materials used as additives, their quantities, and the heating conditions, the contaminated soil could potentially be converted into products that can be used industrially. The dependence of the performance of the CFM process—specifically, the Cs removal rate, minimum heating temperature required, and the final products—on the nature and quantity of the additives is currently being investigated systematically.

## CONCLUSIONS

In this study, we have investigated the Cs removal rate and the structural change of Cs-absorbed weathered biotite (WB) by heating it with mixed salt. The Cs removal rate reached 100% by heating at 700 °C. Structure analyses revealed complete decomposition of WB and formation of augite and several new phases at 700 °C. The complete removal of Cs from the specimen was ascribed to the refusal of these new phases to incorporate Cs with a large ionic radius. We believe that this concept, named cesium-free mineralization (CFM), is promising for decontamination of the radioactive soil in Fukushima.
MATERIALS AND METHODS

WB for the experiment was collected from outcrops in Onotown, Fukushima prefecture. The WB was ground to a fine powder, and particles smaller than 1.8 μm were screened. The difference between the structures of WB and vermiculite has already been reported by Motokawa et al.\textsuperscript{17} Cs sorption was performed according to a well-known method. First, clay minerals were dispersed into a 1.0 × 10⁻³ mol L⁻¹ CsCl solution for 24 h with slow stirring. The sample was then washed repeatedly with distilled water until no free Cl was detected using silver nitrate. The sample was then dried using a freeze-drying machine. The concentration of Cs in the WB samples was 0.8 wt %, as determined by the XRF analysis.

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**Figure 2.** (a) XRD patterns of WB after heat treatment at several temperatures. (b) Mineralogical analysis of the XRD pattern at 700 °C. (c) TEM image of WB after heat treatment at 700 °C. (d) Selected area electron diffraction (SAED) pattern of the crystallite indicated by the arrow in (c) and (e) calculated pattern of augite along [10T].

**Figure 3.** (a) Crystal structure of augite viewed perpendicular to the (001) plane. The blue, yellow, and green polyhedrons are corresponding to T, M1, and M2 sites, respectively. (b) Comparison of ionic radii of several cations for the octahedral coordination, according to Shannon and Prewitt.\textsuperscript{14}
We initially added 40 mg of NaCl–CaCl₂ mixed salt with a molar ratio of 1:1 to 40 mg of WB powder and placed the sample onto a Pt sample plate. We then added several drops of water to the mixture and dried it by heating at approximately 80 °C. The Pt sample plate was heat-treated at temperatures of 400, 500, 600, and 700 °C for 2 h under a reduced pressure of 14 Pa. After natural cooling, the sample was dispersed in 10 mL of distilled water by ultrasonication. It was then subjected to centrifugal separation at 4000 rpm for 30 min. After the supernatant liquid was removed, the sediment was dried on a hot plate at approximately 100 °C.

Composition analysis of the sample was performed on a wavelength-dispersion-type XRF spectrometer (Rigaku RINT2500HLB) using Ni-filtered Cu Kα radiation. In addition, TEM analysis (JEOL, JEM-2010 operated at 200 kV) was used to identify the mineral phases.

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**Notes**

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