Evaluation of Removal Behavior of Cesium in Contaminated Soil Based on Speciation Analysis

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The removal efficiency of Cs from contaminated soil depends on its chemical species bound with the soil components. Therefore, in this study, we observed the elution behavior of Cs based on speciation analysis in a Cs removal experiment conducted on contaminated soils. The treatment method was optimized using simulated contaminated soil and applied to actual contaminated soil on a large scale as well. The elution rate of Cs was approximately 50% or more in both actual and simulated contaminated soil using the optimized treatment method. From the obtained results, a robust treatment method using an eluting reagent and a magnetic adsorbent with low energy costs is proposed. Additionally, the usefulness of speciation analysis in decontamination studies was confirmed.

Keywords Speciation analysis, sequential extraction procedures, Cs-contaminated soil, removal behavior

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Introduction

The accident at the Fukushima Daiichi nuclear power plant in March 2011 polluted extensive areas in Fukushima prefecture and the surrounding areas with radionuclides. It is difficult to reduce the radioactive level in the land area owing to the strong adsorption of radionuclides, especially 134,137Cs, into the soil.1-3 Therefore, surface soil with a high radioactive level in the land area is being shaved, and the contaminated soil is then stored at temporal storage sites, and then moved to an intermediate storage facility. However, an efficient treatment method for this large amount of contaminated soil has not yet been developed.

Many studies on the decontamination of Cs from contaminated soil have been conducted. These studies have been performed using various methods, experimental conditions, and soil samples.4-10 However, the diversity of the decontamination studies makes it difficult to compare the effectiveness of these treatment methods. In particular, when different soil samples were used, different results were obtained, even under similar treatment condition.

The different soil samples have different soil compositions, depending on the sampling site, and this greatly affects the adsorption and dissolution behaviors of Cs.11 Because the chemical species of Cs are different, depending on the soil components in which they are adsorbed, an effective treatment method should be selected based on the soil composition. Other factors affecting the removal effectiveness of Cs are whether the soil sample is simulated contaminated soil with non-radioactive 133Cs or actual contaminated soil with radioactive 134,137Cs and whether the treatment is laboratory scale (g scale) or large scale (kg scale).

It is therefore not adequate to evaluate the treatment methods with the various backgrounds by only using the Cs removal rate. Thus, it is necessary to not only compare the total elution amount of Cs, but also to obtain information on the species of Cs that will be effectively eluted. The analysis of the chemical species of Cs in soil can be evaluated by sequential extraction procedures.12,13 By comparing the amount of Cs in each chemical species before and after treatment, the effectiveness of the treatment on each chemical species of Cs can be determined. Therefore, analyzing the chemical species of Cs is also useful for optimizing the conditions of the elution method and for evaluating the difference in the elution behavior of Cs between different soil samples.

In this study, we observed the Cs elution behavior based on an analysis of the chemical species of Cs in soil by sequential extraction procedures. To ensure the lowest energy cost, we employed the methods of elution by organic acids under ambient conditions.
conditions and magnetic adsorption removal. The elution of Cs in soils with organic acids having a chelation ability for metal ions has been reported. However, the chelation ability of organic acids for alkali metals containing Cs is generally weak, and thus the mechanism of Cs elution by organic acids remains unclear. We hypothesized that the organic acids would act on the components of an adsorption site in Cs, rather than Cs directly, and sought to elucidate the elution mechanism using speciation analysis. Furthermore, the treatment procedure was performed on two kinds of soil samples (simulated contaminated soil and actual contaminated soil), with different treatment scales (lab. scale and large scale).

**Experimental**

**Materials**
All reagents used in this study were of analysis grade and purchased from Wako Pure Chemical Industry Co. Ltd., Japan.

**Pretreatment of soil sample**
The simulant soil used in the Cs elution experiment was obtained from a farm in Minamisoma City in Fukushima prefecture, Japan. The soil contained low levels of radioactive species and consisted of 10.9(±4.6)% organic matter, 52.6(±3.3)% sand, and 36.5(±1.7)% silt and clay. The soil was dried in air and then dried in an oven at 60°C for 2 days. The dried soil was crushed and the larger grains (>2 mm) removed by a sieve. Finally, the natural magnetic minerals in the soil were separated and removed by an Nd-Fe-B magnetic rod (1.4 T, 20 mm diameter x 100 mm length).

The simulant soil was doped with non-radioactive 134,137Cs, then 25 mL of deionized water (DW) was added to 5.0 g of the soil sample, and the mixture was shaken for 10 min, after which 0.5 mL of a Cs solution (10 mg L−1) was added to the mixture and the mixture was then shaken for 1 h. The Cs solution was prepared by diluting a standard cesium gas (99.999%), after filtration and dilution.

The simulated contaminated soil was built and an attempt was made to treat the contaminated soil using a magnetic adsorbent of Prussian blue modified magnetite (PB-mag). After 10 mg of PB-mag was added to 10 mL of the eluent obtained in the treatment with the OA-AA system and the mixture was shaken at room temperature, the PB-mag was collected by an Nd-Fe-B magnet (0.4 T, 25 × 10 × 5 mm). The Cs adsorbed on the PB-mag was eluted by shaking the PB-mag for 30 min in 10 mL of a 2 mM 4H EDTA-free acid solution (adjusted to pH 11.5 with a NaOH solution). After the residual magnetic particles were collected by a magnet, the obtained supernatant was diluted and adjusted at pH 1 with HNO3 and provided for ICP-MS measurements.

**Elution behavior of Cs with organic acids from simulated contaminated soil**

For comparing the elution efficiencies of Cs with various organic acids, 5 g of the simulated contaminated soil was added into 25 mL of 0.5 M organic acid solutions (citric acid, ethylenediaminetetraacetic acid (EDTA), tartaric acid, succinic acid, and ascorbic acid) under various pH conditions, and the mixtures were shaken for 48 h. After shaking, the supernatant was separated from the solid matrix by centrifugation. The concentration of 134Cs in the obtained solutions was measured by ICP-MS.

To evaluate the elution efficiency of Cs with an elution method combining oxalic acid and AcONH4, (thereafter referred to as the OA-AA elution system), 5 g of the simulated contaminated soil was added into 25 mL of a 0.5 M oxalic acid solution, and the mixture was shaken for 48 h. After removing the supernatant by centrifugation, the residual soil was added into 25 mL of a 1 M AcONH4 solution (pH 5.0) and the mixture was shaken for 24 h. The series of the processes, as described above, was repeated twice, and the obtained soil was analyzed using sequential extraction procedures. In addition, for a comparison, analysis by sequential extraction procedures was also performed using the soil that had been eluted with only oxalic acid twice.

**Removal of Cs from the eluent by a magnetic adsorbent**
The Cs in the eluent was removed from the simulated contaminated soil using a magnetic adsorbent of Prussian blue modified magnetite (PB-mag). After 10 mg of PB-mag was added to 10 mL of the eluent obtained in the treatment with the OA-AA system and the mixture was shaken at room temperature, the PB-mag was collected by a magnet, the obtained supernatant was diluted and adjusted at pH 1 with HNO3 and provided for ICP-MS measurements.

**Elution of Cs from the simulated contaminated soil**

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**Results and Discussion**

**Elution behavior of Cs with organic acids from simulated contaminated soil**
The elution of Cs adsorbed in the soil is important as the first process for the removal of radioactive cesium from contaminated...
soil. In order to optimize the Cs elution conditions, the elution amount of Cs was compared under various elution conditions with different organic acids and pH values. Furthermore, the elution behavior of Cs was evaluated in detail by analyzing the chemical species of Cs in the soil before and after an elution treatment using sequential extraction procedures.

Studies have reported that some organic acids having a chelating ability are more effective for the elution of Cs in soil than inorganic acids, such as hydrochloric acid and nitric acid with the same concentration. The elution amounts of Cs with organic acids under strong acidic conditions for the elution of Cs in soil. Therefore, we added new Cs to prepare a simulated contaminated soil, wherein the total amount of Cs was 2.67 mg kg⁻¹ and included chemical species apart from F5. The Cs classified in F5 corresponded to 60% of the total abundance of Cs in the simulated contaminated soil. The speciation pattern of Cs in our simulant was similar to that of soils described in previous reports.

The organic acids, other than oxalic acid, could elute Cs species of F1, 2, and 3 under weak acidic to weak basic conditions (i.e., pH > pK,a1) (Fig. 2). The elution behavior of Cs with tartaric acid (pH 6) was similar to that with EDTA (pH 4), although EDTA generally has a higher chelating ability for most metal ions than tartaric acid. Therefore, this suggests that the contribution of chelate formation in the elution of Cs is not significant. In addition, the eluents contained large amounts of ammonium ions derived from the aqueous ammonia used for adjusting the pH, which could act as an eluent for Cs in F1 and 2 in the sequential extraction procedures. Therefore, the elution of Cs in F3 might be due to the solubilization of Fe and Mn by chelate formation with the organic acids.

Oxalic acid could effectively elute Cs in the F5 that was generally difficult to elute. The 0.5 M oxalic acid solution is a strong acidic condition and exhibits a pH of 0.9. It was suggested that the elution of Cs in the F5 with oxalic acid was caused by its strong acidity or some effect of oxalic acid molecules. To clarify this, the pH of the solution was fixed at 0.9 and the oxalic acid concentration was changed. An increase in the elution amount of Cs was observed as the oxalic acid concentration increased (Fig. S4). In addition, tartaric acid could not elute the Cs in F5 at a pH of 6.0, but could slightly elute it at a pH of 0.9. Therefore, it is important to maintain the chelating ability of organic acids under strong acidic conditions for the elution of

Fig. 1  Elution efficiency of Cs from the simulated contaminated soil by various eluents and pH conditions.

Fig. 2  Fraction analysis of Cs in the simulated contaminated soil before and after the elution process using organic acids.
Cs in F5. According to the acid dissociation equilibrium equation, the abundance ratio of ionic oxalic acid under the condition of a pH of 0.9 is about 30%, and some parts of the oxalic acid exist in their ionic form. For this reason, oxalic acid still has chelating ability at a pH of 0.9, which also contributes to the elution of Cs in F5. On the other hand, the abundance ratio of ionic tartaric acid was about 0.5% at a pH of 0.9. This clearly shows that the amount of Cs in F5 eluted with tartaric acid is much less than that with oxalic acid.

Clay minerals of 2:1 type, smectite, vermiculite, and biotite, consisting of two tetrahedral sheets of silicate, and one octahedral sheet of Al and/or Mg ions have negatively charged cavities, which bound with Cs ions.16 These metal ions of Si, Al and Mg can form a chelate with oxalic acid.17 It was speculated that the oxalic acid treatment would solubilize Al and Mg ions in clay minerals by chelating, and consequently disrupt the structure of clay minerals to elute Cs ions. In fact, when the concentration of Al ions in the solution was measured during an oxalic acid treatment of the simulated contaminated soil, the elution of Al ions was observed (Fig. S5). Therefore, it was confirmed that the oxalic acid treatment could elute Cs in F5 by disrupting the clay structure. It is ideal that the soil treatment can be conducted under mild conditions and with the high efficiency, but no such method has been developed until now. Therefore, we put the priority on the efficiency of Cs removal rather than the mild condition in the treatment method. Oxalic acid elutes Cs of F5 more efficiently than the mild condition, and thus oxalic acid was used as the elution reagent in our method. However, the amount of Cs in F1 and 2 clearly increased more than that before the elution treatment, which seemed to be caused by re-adsorption of the eluted Cs in F5.

Preventing re-adsorption of Cs by the elution system combining oxalic acid and ammonium acetate

Although the elution amount of Cs in F5 by the oxalic acid treatment was approximately 10%, because the eluted Cs from F5 re-adsorbed on the clay mineral as F1 and 2. Therefore, for a highly efficient elution of Cs it is necessary to prevent re-adsorption of the eluted Cs. One of the methods for preventing the re-adsorption of Cs is to use an eluent for the Cs in F1 and 2.

The eluent for the Cs in F1 and 2 in the sequential extraction procedures was AcONH4. It was expected that the addition of AcONH4 could prevent the re-adsorption of Cs eluted from F5 to F1 and 2. In fact, when AcONH4 was added after a treatment with oxalic acid, the abundance of the Cs in F1 and 2 was almost the same as that before the elution treatment, and re-adsorption could be prevented (Fig. 3).

However, a treatment with AcONH4 following oxalic acid could hardly elute the Cs in F1 and 2 already adsorbed before the treatment. There are two possible causes for the low elution efficiency of Cs. The first cause is that most parts of the added ammonium ion were used to form a salt with the unreacted oxalic acid, and a sufficiently high concentration of the ammonium ion for eluting the Cs in F1 and 2 was not maintained. The second cause is that the pH conditions when AcONH4 was added were not suitable for the elution of Cs in F1 and 2. In the sequential extraction procedures, the conditions suitable for the elution of Cs in F1 and 2 were at pH 7 and 5, respectively. However, the pH of the solution was low, even after the treatment of AcONH4 following oxalic acid. From these facts, it might be effective to increase the AcONH4 concentration and/or gradually increase the pH to 7 after adding AcONH4 in order to elute Cs in the F1 and 2, which was already adsorbed.
An adsorption experiment of Cs by a PB-mag in an oxalic acid–AcONH₄ treatment solution was carried out; 90% or more of Cs could be adsorbed and removed (Fig. 4b). Although the adsorption rate of Cs on PB-mag slightly decreased due to competition with high concentrations of ammonium ions, PB-mag retained the high Cs adsorption capacity.

Elution behavior of Cs from actual contaminated soil on a large scale

On the lab scale, sequential processes of elution, prevention of re-adsorption, and adsorption removal for the Cs in the simulated contaminated soil could be performed successfully. Next, we tried to treat actual contaminated soil with radioactive Cs on a large scale. The amount of Cs in the contaminated soil before and after elution was analyzed by the sequential extraction procedures (Fig. 5), and the differences between the Cs elution behavior of the simulated contaminated soil and that of the actual contaminated soil was evaluated.

A large-scale treatment was carried out under the condition where the treatment condition established using the simulated contaminated soil was slightly arranged. It was considered difficult to elute the Cs bound with organic matter, F4, under a condition that was determined using simulated contaminated soil containing a slight amount of organic matter. The Cs in F4 might exist somewhat in actual contaminated soil, so hydrogen peroxide was added after the oxalic acid treatment according to the sequential extraction procedures. After the elution treatment and the adsorption removal treatment, both the intensity of the $^{134}$Cs and $^{137}$Cs derived from the radioactivity in the contaminated soil decreased to less than 50% of the initial value.

As per the results by the sequential extraction procedures, Cs decreased for all fractions other than F3. For Cs in F5, the amount of eluted Cs in the actual contaminated soil increased, compared to that of the simulated contaminated soil. Since there was no increase in the Cs of F1 and 2, owing to re-adsorption, the effectiveness of the AcONH₄ treatment and adsorption removal by PB-mag was confirmed. In addition, the hydrogen peroxide treatment was effective to some extent because the Cs of F4 was also reduced slightly.

For Cs in F3, the amount of Cs in the actual contaminated soil increased after the treatment. In sequential extraction procedures, a reducing agent, hydroxylamine hydrochloride, was used as an eluent for Cs in F3. The increase of Cs of F3 in the soil may be attributed to new iron/manganese oxide binding sites produced by the addition of the oxidizing agent, hydrogen peroxide.

Conclusions

In this study, a treatment method of Cs in soil was optimized using simulated contaminated soil, and applied to actual contaminated soil on a large scale. We examined a treatment method based on two processes, an elution process with organic acid and a removal process by using a magnetic adsorbent. The elution behavior of Cs by various organic acids using simulated contaminated soil was evaluated based on an analysis of the chemical species of Cs by sequential extraction.
In addition, AcONH₄ played an important role in protecting PB-mag, completely prevented the re-adsorption of the eluted Cs. AcONH₄ used as the eluent completely prevented the re-adsorption of the eluted Cs. In addition, AcONH₄ played an important role in protecting PB-mag from excess oxalic acid, and made it possible to adsorb and remove Cs by the PB-mag.

By applying the treatment method combining elution with adsorption removal to the actual contaminated soil on a large scale, more than 50% of radioactive Cs in the soil was removed, and the main species of Cs removed was of F5 at a low energy cost. The obtained results were similar to those of the simulated contaminated soil in terms of the removal efficiency and the elution behavior. This means that the combined method could be conducted without being affected by differences in the soil composition, and the scale of the treatment between the simulated and actual contaminated soil. It is widely applicable to contaminated soils regardless of the difference in the soil compositions. Furthermore, by repeating the operation of this method, a higher removal efficiency is expected. However, this treatment method requires a large amount of reagent, and it is thus necessary to improve our method further to allow practical use.

This study also showed that the analysis of chemical species of Cs was effective in decontamination studies of soil containing radioactive Cs. Because the analysis can visualize the elution behavior of Cs depending on the soil composition, it is indispensable not only for monitoring studies, but also for decontamination studies. It is expected that analysis of the chemical species of Cs in diverse soils under various conditions will lead to the development of practical decontamination methods for radioactive species.

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Supporting Information

The detailed description of sequential extraction procedures, the schematic image and the photographs of the large-scale treatment system, the elution results of Cs depending on oxalic acid, the elution results of Al ion during the treatment of the simulated soil with oxalic acid are located in Supporting Information. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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