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Short Original Communication

Extraction of Cs bound with biotite by addition of oxalic acid without heating

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Abstract

Purpose

There is a large quantity of contaminated soil with radionuclides due to the accident of Fukushima Daiichi Nuclear Power Plant in Japan. Some previous studies reported that Cs^+ could be desorbed from soil with high efficiency, however, these methods required huge input energy for operating. Therefore, we focused on oxalic acid, which has shown relatively high desorption efficiency in previous thermal treatment, and evaluated the potential of oxalic acid as a leaching reagent to reduce the volume of contaminated soil without heating.

Methods

Stable isotope Cs^+ contaminated biotite was retained in plastic bag for 3 months for aging. Oxalic acid was added to the contaminated biotite and the mixture was maintained around 20 °C. After each leaching time, the mixture was separated using filter paper and the concentration of Cs^+ in filtrate was measured. Structural changes in biotite before and after leaching were also analyzed. $LiNO_3$ was also used for comparison studies.

Results

The desorption efficiency of Cs^+ from biotite by leaching with oxalic acid was 94.9% after 2 weeks and the intensity of the specific reflection for biotite in the X-ray diffractograms decreased with leaching time. These results indicate that oxalic acid can remove Cs^+ from biotite through the decomposition of the biotite structure. Since $LiNO_3$ desorbed only 32.2% of Cs^+ as ion-exchangeable form after 2 weeks, oxalic acid can desorb Cs^+, which has a strong interaction with biotite such as the inner-sphere complex, without heating.

Conclusion

Although the desorption of Cs^+ from biotite by leaching with oxalic acid leaching takes a long time, it is a great advantage that this leaching method does not require external energy such as heating. Therefore, oxalic acid leaching has high potential to reduce the volume of contaminated soil with radionuclides.

Keywords: Cesium desorption; Biotite; Oxalic acid leaching; Decomposition; Without heating; Volume reduction

1 Introduction

The accident at the Fukushima Daiichi Nuclear Power Plant happened in Japan on March 2011. The quantity of contaminated soil was estimated to be 13-14 million m^3, of which the clayey soil discharged from agricultural fields and forests was estimated to be 6 million m^3 (Japan Ministry of the Environment, 2019). The transportation of these soils from the temporary storage site to the interim storage facility started in 2015 (Japan Ministry of the Environment, 2018). It is estimated that even after a ^{137}Cs half-life of 30 years, the volume of soil above 8,000 Bq/kg will be 105 thousand m^3, of which 98 thousand m^3 is clayey soil (Japan Ministry of the Environment, 2018). The contaminated soils with less than 8,000 Bq/kg are intended to be recycled as inorganic civil engineering material, while the contaminated soils with more than 8,000 Bq/kg are difficult to utilize as resources. In Japan where there are many natural disasters, the safe storage of the large quantity of contaminated soil for a long time is limited. Therefore, the removal of radioactive Cs from contaminated soil is urgently needed to reduce the volume of contaminated soil. However, Cs$^+$ forms an inner-sphere complex, which directly coordinates without the intervention of water molecules, with the interlayers of clay minerals, and this interaction is too strong to separate Cs$^+$ from clay minerals (Mukai et al. 2018). Recently, low-pressure sublimation, thermal, and microwave treatments have been developed to desorb Cs$^+$ from the contaminated soil (Shimoyama et al. 2014; Parajuli et al. 2015; Yin et al. 2017; Tamura et al. 2021; Akemoto et al. 2021a). These methods have high desorption efficiency of Cs$^+$ from soil in relatively short time, however, heating at the boiling point of water or more is required.

Therefore, these method have limits to treat with large quantity of contaminated soil.

In this study, we focused on oxalic acid which has relatively high desorption efficiency in previous thermal treatment without a special experimental environment (Kim et al. 2020). The potential of oxalic acid was evaluated by the desorption experiment of Cs^+ from model contaminated biotite without heating.

2 Materials and methods

2.1 Clay mineral and reagents

Biotite in Tamura-gun, Fukushima Prefecture, Japan (Geo-Science Materials Nichika Inc., Japan) was used as the model clay mineral. Since the adsorption behavior of Cs^+ on this biotite was established by the Freundlich adsorption isotherm, the interlayer and surface of biotite acted as adsorption sites for Cs^+ (Akemoto et al. 2021b). For characteristics of biotite used in this study, cation exchange capacity is 380 mmol/kg and chemical component is shown in **Table S1**. From the K_2O content in the biotite, the biotite used in our study is suggested to be more weathering and then it may be difficult to desorb Cs^+ from the biotite by the ordinal condition (Kitayama et al. 2020). Cesium chloride (guaranteed reagent grade, >99%) and oxalic acid (guaranteed reagent grade, 98%) were purchased from Fujifilm Wako Pure Chemical Corporation, Japan. Lithium nitrate (guaranteed reagent grade, >98%) was purchased from Kanto Chemical Co., Inc., Japan. All reagents were used without pretreatment.

2.2 Desorption experiment

The Cs^+ contaminated biotite was prepared as described in a previous study (Akemoto et al. 2021b). The particle size of biotite was less than 53 μm and the adsorption capacity of biotite for Cs^+ was 31.9 mg/g. Biotite that adsorbed Cs^+ was retained in plastic bag at room temperature for 3 months before experiments. Oxalic acid (0.5 mol/L, 25 mL) was added to the contaminated biotite (0.05 g) and the mixture was maintained without any mechanical shaking under room temperature, which was measured continuously during the experiment (Thermo Recorder, TR-71U, T&D Corporation, Japan). After each leaching time (1 hour, 1 day, 3 days, 1 week, 2 weeks, 3 weeks, and 4 weeks), the mixture was separated using a filter paper (5C, 1 μm pore size, Toyo Roshi Kaisha Ltd., Japan), and the concentration of Cs^+ in the filtrate was measured using a flame atomic absorption spectrophotometer (FAAS, ZA-3300, Hitachi Ltd., Japan) at 852.1 nm. Oxalic acid at low concentration (0.1 mol/L) and $LiNO_3$ (1.0 mol/L) were also used for comparison studies for their effect on extraction of Cs^+ with the same methodology as mentioned above. Since Li^+ has a high hydration energy, it is expected to desorb Cs^+ by expansion of the clay mineral interlayer due to the penetration of Li^+ in it (Mukai et al. 2018). The desorption efficiency of Cs^+ from biotite was calculated by the following equation (**Eq. 1**).

$$\text{Desorption efficiency (\%)} = \frac{C_t \times V}{Q \times W} \times 100 \qquad (1)$$

where C_t is the concentration of Cs^+ (mg/L) in the solution after each leaching time t, V is the volume of the extract solution (L), Q is the adsorption capacity of biotite for Cs^+ (31.9 mg/g), and W is the amount of biotite (g). All experiments were performed in triplicates. The main elements of the clay minerals (Al, Fe, Mg, and Si) in the filtrate were measured using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ICPS-8100, Shimadzu Corporation, Japan). The percentage of these elements (Al, Fe, Mg, and Si) extracted from the initial biotite was calculated based on the results of energy-dispersive X-ray fluorescence spectrometry (XRF, JSX-3100RII, JEOL Ltd., Japan) (Akemoto et al. 2021b). The solution pH was measured using a pH meter (D-51, Horiba Ltd., Japan). The biotite before and after leaching treatment was measured using powder X-ray diffraction (XRD, SmartLab, Rigaku Corporation, Japan). XRD was performed using Cu Kα radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA at a speed of 1 °/min and an angular step of 0.01°.

3 Results and discussion

The room temperature was observed to be at 20 ± 5 °C during the 4 weeks experiment. The pH of the solutions were 5.9, 1.3 and 0.8 in 1.0 mol/L $LiNO_3$, 0.1 mol/L oxalic acid and 0.5 mol/L oxalic acid, respectively, and these values were consistent throughout the experiment. The Cs^+ adsorbed on clay minerals is considered to mainly take two forms (Fan et al. 2014). One is the outer-sphere complex on the interlayer or planar site, and this form is relatively easy to desorb by alkali metal ions. The other cannot be desorbed easily due to the formation of the inner-sphere complex on the interlayer or frayed edge site. The Cs^+, which was not desorbed by Li^+, was considered to exist as an inner-sphere complex in biotite.

Figure 1 shows the desorption efficiency of Cs^+ from biotite at each leaching time. $LiNO_3$ could desorb approximately 31.6% of Cs^+ after 1 h of leaching time, and the desorption efficiency was consistent throughout the experiment. According to a previous study, approximately 40% of Cs^+ in biotite is existed as an ion-exchangeable form (Akemoto et al. 2021b). In this study, Li^+ desorbed the ion-exchangeable form of Cs^+ from biotite and reached equilibrium within 1 h of the leaching time.

The desorption efficiency by oxalic acid increased with leaching time, and the value of 85.3% (0.1 mol/L) and 94.9% (0.5 mol/L) were obtained after 2 weeks, and 89.8% (0.1 mol/L) and 96.1% (0.5 mol/L) were obtained after 4 weeks of the experiment. These efficiencies were higher than that of Li^+. The Cs^+ has been considered to move into the interlayer of clay minerals and retain in an energy-stable site (Mukai et al. 2018). Since this study used biotite that has been saturated with Cs^+ and aged for 3 months, Cs^+ could have occupied the energy-stable sites that were inaccessible. Therefore, the high efficiency of oxalic acid can be attributed to the ability of oxalic acid to desorb Cs^+ in both outer-sphere complex and inner-sphere complex with biotite.

Al, Mg, Fe, and Si are the main components of clay minerals, and the concentrations of each element in the extract solution was measured as a function of leaching time. When $LiNO_3$ was used as an extraction solution, Al, Mg, Fe, and Si was hardly observed in the solution (**Fig. S1**). **Figure 3a** indicates X-ray diffractograms of biotite after each leaching time by $LiNO_3$. The basal spacing of biotite after Cs^+ was 1.0 nm ($2\theta = 8.7°$), indicating that Cs^+ was still adsorbed in the interlayer (Kogure et al. 2012). The intensity of this reflection (8.7°) was consistent even after 4 weeks, the biotite structure was unaltered. This result also indicated that $LiNO_3$ desorbed only Cs^+ in an ion-exchangeable form. In contrast, oxalic acid desorbed Al, Mg, Fe, and Si in the biotite. The desorption rates of Al, Mg, and Fe were 68%, 83%, and 94% by 0.5 mol/L oxalic acid after 2 weeks, and this desorption rate did not significantly change until 4 weeks (**Fig. 2**). Since the desorption efficiency of Cs^+ by 0.5 mol/L oxalic acid also plateaued at a leaching time of 2 weeks (**Fig. 1**), these results indicate that the decomposition of clay minerals by oxalic acid (0.5 mol/L) induced the desorption of Cs^+ from biotite at room temperature. When oxalic acid was 0.1 mol/L, the concentrations of Al, Mg, and Fe continued to increase even after 4 weeks (**Fig. S1**). At 4 weeks of leaching time, the desorption rates of Al, Mg, and Fe were 60%, 78%, and 91%, respectively.

Buckwheat has been reported to detoxify Al with oxalic acid released from its root, which forms an oxalate complex, with Al to oxalic acid ratio of 1:3 (Ma et al. 1997). The reaction ratio between Fe and oxalic acid was 2:5 (Lee et al. 2006). The concentration of Al and Fe in biotite used in this study was 3.2 mmol/g and 2.0 mmol/g, respectively. Therefore, even 0.1 mol/L of oxalic acid was sufficient to react with all Al and Fe to form their complexes with oxalic acid. The XRD results indicated that the intensity of the biotite reflection decreased with leaching time (**Figs. 3b and 3c**), although this biotite reflection (1.0 nm) has not completely disappeared with 0.1 mol/L of oxalic acid, even at a leaching time of 4 weeks (**Fig. 3b**). This result implied that the decomposition of biotite by 0.1 mol/L oxalic acid takes long time over 4 weeks. On the other hand, it was almost completely disappeared with 0.5 mol/L oxalic acid after 2 weeks (**Fig. 3c**).

The broad peak around 11.5 ° was estimated to be oriented from a hydrotalcite-like structure, which has XRD reflection at 11.7 ° and is similar to octahedral sheet (Miyata 1983; Bernard et al. 2022). Assuming that Al and Fe eluted by oxalic acid leaching are metals that have existed in the tetrahedral sheet by isomorphous substitute with Si, it is considered that the tetrahedral sheet could not maintain its structure due to this elution. Since this reflection appears with the decrease in biotite reflection, it is presumed to be from the remaining octahedral sheet. These results indicated that oxalic acid (0.5 mol/L) could desorb elements (Al, Mg, Fe, and Si) in biotite and consequently decompose its structure. The The Cs^+ desorption from biotite due to decomposition of its structure by oxalic acid can be performed even without heating.

Oxalic acid is a natural organic acid present in various plants and is highly effective in the field of environmental remediation (Huang et al. 2021; Costa et al. 2022). Since the results of this study confirmed that Cs^+ strongly bound in clay minerals can be desorbed with oxalic acid without heating, there is the possibility of introducing plants with oxalic acid content as a soil remediation technology option. Moreover, this oxalic acid leaching has the potential to be a low energy soil remediation as it does not require heating.

4 Conclusions

In this study, the Cs^+ desorption from biotite using oxalic acid was investigated without heating. Oxalic acid (0.5 mol/L) could desorb Cs^+ from biotite which has been aged for 3 months, and its desorption efficiency was 94.9% after 2 weeks. In the same procedure, $LiNO_3$ could desorb only 32.2% of Cs^+ after 2 weeks. These results indicate the ability of oxalic acid to desorb Cs^+ from biotite not only the outer-sphere complex like ion-exchangeable form but also the inner-sphere complex. Although the desorption of Cs^+ from biotite by oxalic acid leaching takes a long time (at least 2 weeks), the fact that no external energy is required for extraction is a great advantage. Therefore, oxalic acid leaching without heating can be used for the volume reduction of contaminated soil with radionuclides.

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Author contribution

Yasuhiro Akemoto: Conceptualization, Methodology, Formal analysis and investigation, Writing - original draft preparation, Visualization

Seira Takahashi: Methodology, Investigation

Toko Iwamura: Methodology, Investigation

Masahiko Kan: Writing - review and editing

Shunitz Tanaka: Methodology, Writing - review and editing, Supervision

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing Interests

The authors declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

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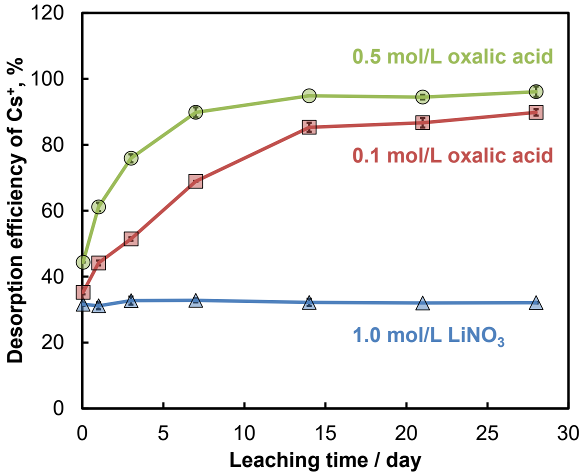
Figure captions

Fig. 1 Desorption efficiency of Cs^+ from biotite at each leaching time at 20 ± 5 °C. Biotite: 0.05 g, the leaching solution: 25 mL. Error bars indicate standard deviation (n = 3)

Fig. 2 Desorption rate of elements at each leaching time from biotite by 0.5 mol/L oxalic acid; Symbols, purple triangle was Fe, blue circle was Mg, red square was Al, and green rhombus was Si, respectively

Fig. 3 XRD patterns of biotite after each leaching treatment, a) 1.0 mol/L $LiNO_3$, b) 0.1 mol/L oxalic acid, c) 0.5 mol/L oxalic acid



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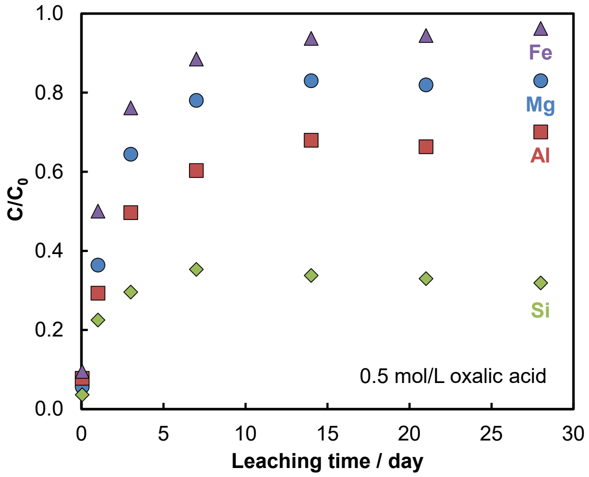

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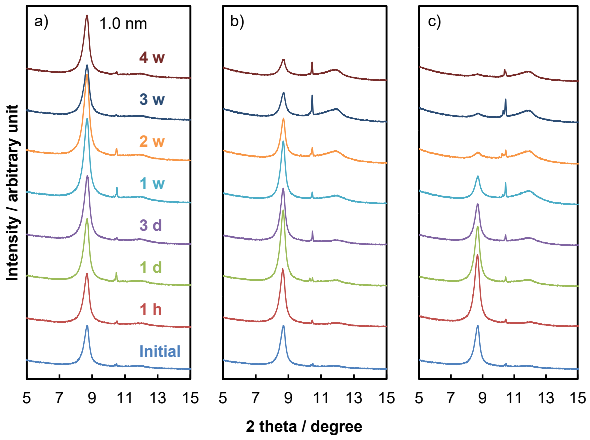

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