

## Original Paper

# Desorption of cesium from Fukushima soils using a mechanochemical method

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## Abstract

The Fukushima Daiichi Nuclear Power Plant accident caused severe soil contamination by radioactive cesium (Cs). The large volume of removed soil from decontamination must be disposed of by 2045, requiring volume reduction. However, Cs is strongly adsorbed onto clay minerals in the soil, making removal difficult. Thus, the desorption behavior of stable Cs adsorbed onto weathered biotite (WB), a clay mineral abundant in Fukushima soils, was investigated using a mechanochemical (MC) method that combines physical grinding by ball impact and friction with a wet process promoting chemical reactions. The effectiveness of this method for desorbing radioactive Cs from Fukushima soil was also evaluated. The results are based on the scanning electron microscopy analysis and the results of the desorption experiment; oxalic acid desorbed Cs to some extent without affecting the layered structure of the clay minerals significantly, and ammonium chloride showed an exfoliation of the layer structure, resulting in a stable desorption of Cs independent of samples. Regarding the real soil samples collected in Fukushima, the MC method using ammonium chloride solution desorbed 80% of <sup>137</sup>Cs, and the desorption behavior was reproduced reliably in actual soil samples. In contrast, oxalic acid did not always result in radioactive Cs made sufficiently desorbed for all the samples. Based on these findings, the MC method with ammonium chloride promotes radioactive Cs desorption effectively from interlayers due to synergistic effects from the layered structure's exfoliation and chemical interaction. The MC method with ammonium chloride should reduce the volume of removed soil requiring final disposal, thereby reducing associated management costs.

**Keywords:** ball milling; interlayer core site; mechanochemical; radioactive cesium; weathered biotite

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## Introduction

The Fukushima Daiichi Nuclear Power Plant accident (2011) released radioactive cesium (<sup>137</sup>Cs and <sup>134</sup>Cs), causing environmental contamination. The total amount of soil affected and removed is estimated to be ~13 million m<sup>3</sup>, consisting of ~7 million m<sup>3</sup> of sandy soil and ~6 million m<sup>3</sup> of clay soil. The soil must be disposed of outside of Fukushima Prefecture by 2045 following storage at the 'Interim Storage Facility' (Ministry of the Environment of Japan, 2019a). To reduce the final disposal volume, the reuse of removed soil is essential, and for this, the concentration of Cs must be kept at <8000 Bq kg<sup>-1</sup> of soil (Ministry of the Environment of Japan, 2019b). The primary radionuclides in the removed soil and waste

stored in the Interim Storage Facility are <sup>137</sup>Cs (half-life: 30 years) and <sup>134</sup>Cs (half-life: 2 years), and their estimated radioactivity after 30 years will be <8000 Bq kg<sup>-1</sup> of soil for >80% of the ~13 million m<sup>3</sup> (Ministry of the Environment of Japan, 2019a). However, high air dose rate and long-term radiation control are problematic for the remaining 20% of the soil and waste that have been removed. Reducing the volume of soil which will still contain >8000 Bq kg<sup>-1</sup> of soil after 2045 is essential for final disposal.

Cesium (Cs) is the heaviest alkaline element on earth with stable isotopes. The alkali elements belong to the group 1 elements of the periodic table and form stable univalent cations with the same electron configuration as that of noble gases by releasing one electron. Previous geochemical studies have shown that Cs can be adsorbed selectively and strongly, and stabilized by clay minerals of <2 µm particle size in soil (Cornell, 1993). In particular, radioautography and transmission electron microscopy experiments showed that Cs was adsorbed selectively on weathered mica minerals (Mukai et al., 2016) in Fukushima Prefecture. The

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edges of 2:1 clay minerals have selective adsorption sites for Cs and K ions, known as frayed edge sites (FES), formed due to water swelling and physical structural degradation caused by weathering (Jackson, 1962; Sawhney, 1972; McKinley *et al.*, 2004; Nakao *et al.*, 2008). The results of empirical experiments visualizing the adsorption sites using radiography have also been reported (McKinley *et al.*, 2001). In a recent report, scraping the edges and other surface areas did not remove radioactive Cs entirely (Mukai *et al.*, 2014) and the radioactive Cs was reported to have adsorbed uniformly not only in the FES but also internally within the clay minerals such as weathered biotite (Mukai *et al.*, 2014; Kikuchi *et al.*, 2015; Park *et al.*, 2019). The results suggest that the distribution of Cs in clay minerals could make its removal challenging. Furthermore, using small-angle X-ray scattering (SAXS) (Motokawa *et al.*, 2014a) and dispersive X-ray absorption fine structure (DXAFS) (Yaita *et al.*, 2016) have demonstrated that Cs entered the interlayer through a mechanism involving internal penetration. As a result, Cs is believed to interact directly with the clay mineral layer, ultimately leading to a chemically irreversible state.

On the other hand, the amount of radioactive Cs adsorbed to the soil around Fukushima is insufficient for direct observation of the chemical state of Cs (Yamasaki and Utsunomiya, 2022). Accurate information about adsorption sites that retain trace amounts of Cs, such as FES (Bradbury and Baeyens, 2000) and within clay minerals (Mukai *et al.*, 2014), is difficult to obtain. Even if the experimental results for stable Cs are applied directly to actual soil, sufficient decontamination for radioactive Cs may not be expected. Consequently, the purpose of the present study was to apply a mechanochemical (MC) method including ball-mill pulverization to the decontamination of Cs, with the expectation that the chemical reagents would reach the interlayer space of the clay minerals efficiently. A further objective was to conduct desorption experiments for radioactive Cs using contaminated soil, and to compare those results with simulation experiments to evaluate the effectiveness of the MC method.

## Materials and methods

### Evaluation of Cs adsorption on clay mineral samples

Weathered biotite (WB) from the Ono-machi Fukushima Prefecture was tested in terms of its potential for desorption of stable Cs (WB provided by Fukushima Vermo Co. Ltd, Fukushima, Japan). The WB sample was described by Motokawa *et al.* (2014b). Clay mineral particles with a grain size of <2 µm were collected via water elutriation and the chemical composition of WB was measured by X-ray fluorescence analysis (XRF; Rigaku ZSX PrimusII, Tokyo, Japan) (Table 1). Samples were prepared using the loose powder method, in which the sample was placed in a plastic container and covered with a polypropylene film. The instrument was operated using a Rh tube at 50 kV and 50 mA. The measurement diameter was 10 mm.

Experiments were conducted to determine the saturated adsorption concentration of Cs on WB, using average values from three experiments. A solution of 20 mL of 0.1 mol L<sup>-1</sup> CsCl was added to 300 mg of WB in a 50 mL polypropylene centrifuge tube; the sample was then stirred end-over-end for 24 h to allow Cs adsorption to occur, based on previous reports indicating that Cs adsorption onto mica minerals reaches apparent equilibrium within day (Murota *et al.*, 2020). After adsorption, the solution was centrifuged (CN-1050, AS ONE Corporation, Tokyo, Japan) at 5000 rpm (relative centrifugal

**Table 1.** Chemical composition (wt.%) of untreated weathered biotite

Elements	Mass %
	WB
SiO <sub>2</sub>	33.7
Fe <sub>2</sub> O <sub>3</sub>	29.6
Al <sub>2</sub> O <sub>3</sub>	16.3
TiO <sub>2</sub>	3.6
MnO	0.34
P <sub>2</sub> O <sub>5</sub>	0.10
CaO	1.1
MgO	8.1
K <sub>2</sub> O	7.1

force [RCF] = 2096 g) for 10 min to separate the solid from the liquid. The supernatant was then filtered through a 0.45 µm membrane filter to remove any residual solid phase from the liquid, and the Cs<sup>+</sup> concentration was determined using inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer NexIon 300D). The amount of Cs adsorbed was calculated using Eqn 1, where C<sub>0</sub> is the initial concentration of Cs (ppm), C is Cs concentration after 24 h equilibrium (ppm), V<sub>L</sub> is the amount of solution (L), and V<sub>m</sub> is mass of clay mineral (g):

$$\text{Amount of Cs adsorbed (mg Cs/g WB)} = (C_0 - C) \times \frac{V_L}{V_m} \quad (1)$$

### Preparation of the Cs-saturated clay mineral samples

To saturate the WB samples with Cs, 1000 mg of WB was placed in a 50 mL centrifuge tube, and 40 mL of 0.1 mol L<sup>-1</sup> CsCl was added and stirred for 12 h. The supernatant solution obtained by centrifugation at 5000 rpm (RCF = 2096 g) for 10 min was discarded and replaced with a fresh solution, which was then stirred for a further 12 h. This treatment to saturate the WB with Cs was performed three times. Distilled water was added to remove the excess salt adhering to the WB after the treatment, and the mixture was washed by shaking by hand. The experimental sample was finally dried in a freeze drier (Yamato Scientific DC-801, Tokyo, Japan) for 24 h and crushed using an agate mortar. The solid obtained was Cs-saturated WB (Cs-WB), which was then used in the Cs desorption experiments.

### Examination of Cs desorption by rotary stirring and MC treatments using various reagents on clay mineral samples

To determine the effect of various reagents on Cs desorption from Cs-WB, samples were reacted with ion-exchange solutions consisting of LiCl (Kanto Chemical guaranteed reagent), NaCl (Wako Chemical special grade), or KCl (Aldrich 99.99+%), i.e. cations belonging to the same alkali group, or alkaline earths MgCl<sub>2</sub> · 6H<sub>2</sub>O, or anhydrous CaCl<sub>2</sub>, or NH<sub>4</sub>Cl, a cation with approximately the same ionic radius as Cs. Desorption by oxalic acid dihydrate (Kanto Chemical particular grade) was investigated also because of its tendency to decompose the structure of clay minerals (Akemoto *et al.*, 2021). Distilled water was also evaluated for comparison. 10 mL of 1.0 M ion-exchange solution was added to 100 mg of Cs-WB in a 15 mL polypropylene centrifuge tube and

stirred in a rotary end-over-end stirrer (Rotamix RKVSD, Towa Lab Co. Ltd, Tokyo, Japan) for 24 or 168 h. The Cs concentration in the supernatant solution (centrifuged after stirring) was measured using ICP-MS and the amount of desorption was calculated from the mean of three repeated experiments. The extent of Cs desorption (%) from the Cs-WB was calculated using Eqn 2, where  $C$  is Cs concentration after stirring for 24 or 168 h (ppm), based on the amount of Cs released into the solution relative to the amount adsorbed on the WB:

$$\text{Amount of Cs desorbed (mg Cs/g WB)} = C \times \frac{V_L}{V_m}$$

Extent of desorption(%) =

$$\left[ \frac{\text{Amount of Cs desorbed (mg Cs/g WB)}}{\text{Amount of Cs adsorbed (mg Cs/g WB)}} \right] \times 100. \quad (2)$$

Physical grinding, referred to herein as MC treatment, was accomplished by solid samples being placed in a planetary rotating ball mill (Ito Seisakusho LP-M2, Tokyo, Japan) in a 45 mL zirconia grinding vessel with 20 mL of 1 mol L<sup>-1</sup> of one of the desorbing ion-exchange solutions (see above), 300 mg of Cs-WB, and 30 g of <2 mm zirconia balls. The ball-mill grinding was thus performed under wet conditions. The mill rotation speed was 400 rpm for 72 h; for oxalic acid the grinding was also performed for 168 h, considering that the longer the treatment time, the greater the clay dissolution. After treatment, the sample was transferred to a 50 mL centrifuge tube, and solid/liquid separation was obtained via centrifugation, as described above. The extent of Cs desorption from Cs-WB was measured by ICP-MS and calculated using Eqn 2.

After the MC treatments, the Cs-WB samples were collected, washed, and dried with distilled water and analyzed using X-ray diffraction (XRD; Rigaku RINT-UltimaIII, Tokyo, Japan) and scanning electron microscopy (SEM; JEOL JSM-IT100, Tokyo, Japan). Before treatment, the Cs-WB was also analyzed by XRD and SEM for comparison. The samples were spread uniformly over a 2.0 cm × 2.7 cm area on quartz glass for XRD measurements. The samples were measured using CuK $\alpha$  operating at 40 kV and 30 mA over the range 2–80°2 $\theta$  with a step size of 0.04°2 $\theta$ . For SEM measurements, a solid sample was adhered to carbon tape attached to the sample stand and sputter-coated with gold. The samples were examined at ×3300 magnification under an acceleration voltage of 15 kV.

#### Assessment of <sup>137</sup>Cs desorption, following MC treatment, from the soil samples collected in Fukushima Prefecture

The desorption of <sup>137</sup>Cs from soil samples by MC treatments was evaluated. According to a map of measured air dose rates at 1 m above the ground in Fukushima and neighboring prefectures (Japan Atomic Energy Agency, 2017), as of 16 November 2017, the area with the greatest concentration of radioactive materials was declared to be northwest of the Fukushima Daiichi Nuclear Power Plant, leading to the selection of clayey soil samples from four different locations in that direction for the experiment. Soil samples A and B were collected on 9 August 2017; sample C on 14 June 2018; and sample D on 24 August 2017.

Soil samples were particle-size fractionated to <2 mm by dry sieving, then placed in 1.5 mL polypropylene tubes filled halfway so that the volume of the sample was constant at the time of measurement. The <sup>137</sup>Cs radioactivity ( $\gamma$  = 661.7 keV) of the soil

samples was measured using a Ge semiconductor detector (Ortec GWL-90-10) linked to a multi-channel analyzer (Seico EG&G MCA-7, Tokyo, Japan) for 6–15 h. In addition, the chemical composition of the Fukushima soil samples was determined by XRF (Table 2). The soil sample after  $\gamma$ -ray spectrometry was ground in the ball mill as before with NH<sub>4</sub>Cl for 12 and 72 h and with oxalic acid for 72 h. For comparison, the same soil sample with NH<sub>4</sub>Cl was placed in a 50 mL centrifuge tube and subjected to 72 h of rotary stirring without the MC treatment.

After milling, this sample was transferred to a 50 mL tube, rinsing the ball-mill container with distilled water as necessary until complete sample transfer was achieved. The sample was judged to be almost completely recovered, as no residue was observed in the reaction vessel. The soil was then washed using 20 mL of distilled water and centrifuged again to remove the excess chemical. The washed soil was transferred to 2 mL tubes, freeze-dried, and utilized for  $\gamma$ -ray spectrometry. From the  $\gamma$ -ray spectrometry of the soil before and after treatment, the extent of <sup>137</sup>Cs desorption was measured and calculated as the average of three experiments using Eqn 3, where  $C_B$  is Cs concentration before treatment (Bq kg<sup>-1</sup> soil), and  $C_A$  is Cs concentration after treatment (Bq kg<sup>-1</sup> soil):

$$\begin{aligned} {}^{137}\text{Cs concentration (Bq/kg soil)} &= \frac{(\text{Counting rate})}{(\text{Counting efficiency} \times \gamma \text{ ray emission ratio})} \times \frac{1000}{\text{mass (g soil)}} \\ \text{Extent of desorption (\%)} &= \frac{(C_B) - (C_A)}{(C_B)} \times 100 \quad (3) \end{aligned}$$

The change in the crystal structure of the soil after treatment was observed from the XRD measurement of the samples after  $\gamma$ -ray spectrometry.

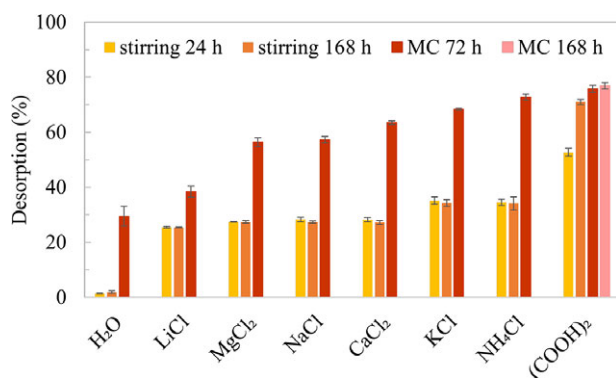
## Results and Discussion

### Desorption time and solutions for Cs desorption after stirring and MC treatment

Adsorption experiments of Cs<sup>+</sup> on <2  $\mu$ m WB obtained via water elutriation confirmed the amount of Cs<sup>+</sup> adsorbed on WB to

**Table 2.** Chemical composition of soil samples from Fukushima before MC treatment

Elements	wt. %			
	A	B	C	D
SiO <sub>2</sub>	56.8	57.2	53.9	48.3
Fe <sub>2</sub> O <sub>3</sub>	8.38	11.7	9.77	14.2
Al <sub>2</sub> O <sub>3</sub>	23.3	21.2	23.1	27.4
TiO <sub>2</sub>	1.06	1.35	1.10	1.58
MnO	0.14	0.21	0.20	0.31
P <sub>2</sub> O <sub>5</sub>	1.32	0.56	2.44	1.82
SO <sub>3</sub>	0.38	0.19	0.94	0.28
Na <sub>2</sub> O	1.53	0.19	0.97	0.41
CaO	2.92	0.89	3.17	2.28
MgO	1.07	0.48	1.37	1.34
K <sub>2</sub> O	3.06	6.14	3.03	2.13



**Figure 1.** Cs desorption under slow rotatory stirring, for 24 h and 168 h, with various reagents, and the results of the Cs desorption after MC treatment for 72 h and 168 h for WB. Error bars equate to standard deviation data for three replicate results.

be 5.4 wt.%. The results of Cs desorption from WB at 24 and 168 h under slow rotary stirring with various reagents and after 72 and 168 h of MC treatment showed the following (Fig. 1): almost no Cs was desorbed with rotary stirring using distilled water. In contrast, when cation-exchange reagents were used, desorption of 25–35% was achieved. No further increase in desorption was observed even after prolonged stirring for 168 h. This indicates that the Cs<sup>+</sup> adsorbed on the surface of the clay minerals was replaced by other cations during the stirring, but not the Cs<sup>+</sup> adsorbed in the interlayers of the clay mineral. On the other hand, with oxalic acid, desorption was ~50% after 24 h and increased further to ~71% after 168 h of stirring due to the dissolution of the minerals under acidic conditions.

The MC treatment with distilled water caused some Cs leaching, probably due to impact, friction, and deformation. Ion-exchange reagents increased Cs desorption through cation exchange with adsorbed Cs<sup>+</sup>. NH<sub>4</sub>Cl led to increased Cs desorption of >73% after 72 h. The MC treatment with oxalic acid resulted in Cs desorption of >76%, greater than stirring, and further improvement in the Cs desorption was not observed from the MC method even after 168 h. Cs desorption tends to be greater for cations with lower hydration energy, which are more easily fixed in the clay mineral interlayers (Sawhney, 1972; Moldoveanu and Papangelakis, 2012). The results showing that NH<sub>4</sub><sup>+</sup> with an ionic radius close to that of Cs<sup>+</sup> had a large effect on Cs<sup>+</sup> desorption were reasonable. On the other hand, oxalic acid, as an acid, promoted desorption by dissolving minerals and eluting Cs, which was thought to have resulted in a desorption behavior different from that of the ion exchange type.

The XRD patterns (Fig. 2) of Cs-WB before the MC treatments with various reagents showed that peaks of WB and kaolinite were observed. The WB peak intensity decreased after 72 h MC treatment of Cs-WB with distilled water. After MC treatment with divalent Mg<sup>2+</sup> and Ca<sup>2+</sup> solutions, the WB peaks decreased in intensity but disappeared completely when treated with monovalent cationic reagents (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and NH<sub>4</sub><sup>+</sup> solutions). In general, milling treatment weakened the X-ray reflection intensity of the clay mineral, indicating the progress of amorphization (Frost *et al.*, 2001; Xia *et al.*, 2010). Furthermore, addition of Li<sup>+</sup> or NH<sub>4</sub><sup>+</sup> to the grinding media can accelerate destruction of the mineral structure (Papirer *et al.*, 1990). Similar to previous reports, ion exchange with cations and ball milling treatment probably destroyed the layered structure of the clay mineral.

On the other hand, the intensity of the kaolinite XRD peak after MC treatment in the presence of oxalic acid decreased after 72 h, confirming the decrease in crystallinity of the clay mineral. A further decrease, however, was not observed after the more

extended 168 h of treatment, with the sample maintaining a slight crystal structure. These results show that the extent of desorption of Cs was almost the same as that of the 72 h MC treatment in the presence of ammonium ions, but also suggested the possibility that the reaction sites on the clay mineral may differ depending on whether the reagent is an acid or cation.

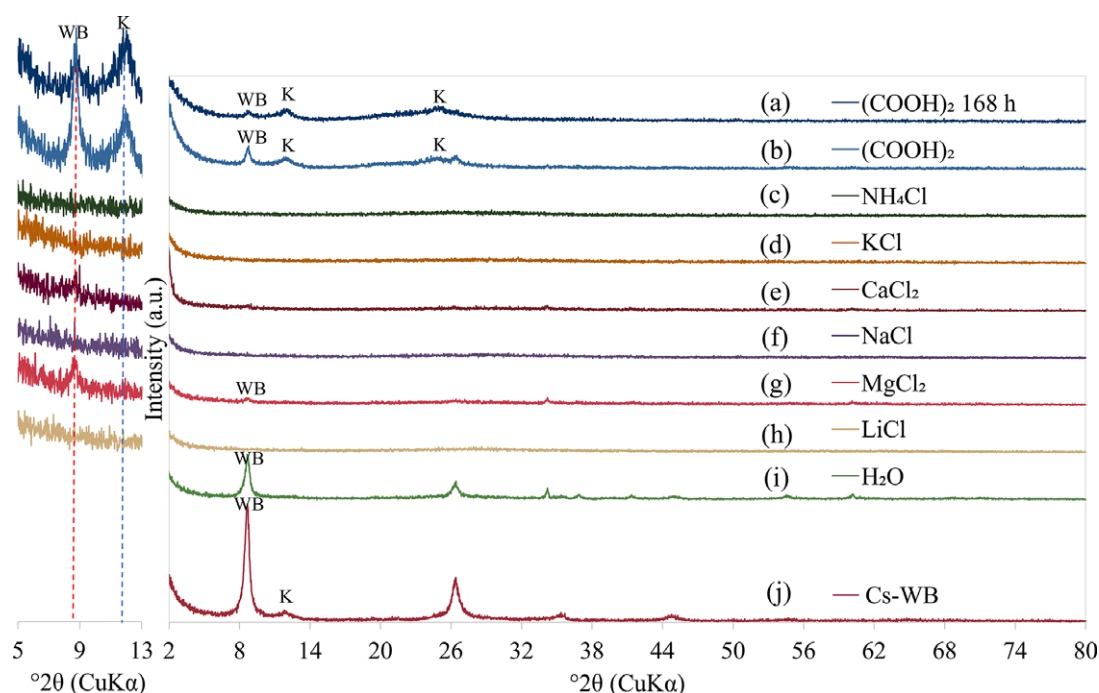
The disappearance of XRD peaks indicates that MC treatments with monovalent cations facilitated amorphization of the clay crystal structure of the clay minerals in a shorter time than treatments with divalent cations or organic acidic solutions. Furthermore, the reason for the lower extent of Cs desorption in the presence of Li<sup>+</sup> and Na<sup>+</sup> solutions, despite amorphization by MC treatment, is that cations with larger ionic radii exhibit greater selectivity in ion exchange, even when the valence is the same (Lee *et al.*, 2017). On the other hand, samples prepared with divalent cation solutions, as seen in the expanded XRD patterns (Fig. 2), showed slight residual peaks due to the reflection of the Cs-WB layer. Despite the lack of amorphization, the greater extent of desorption in the presence of Mg<sup>2+</sup> and Ca<sup>2+</sup> solutions compared with Li<sup>+</sup> solution is attributed to the greater ion exchange selectivity of divalent cations. The greater ionic charge may enhance electrostatic attraction to negatively charged sites on clay minerals. Comparing these results, the effects of valence and ion size on desorption efficiency (Fig. 1), the trends of Cs desorption efficiency were consistent, and the order of Cs desorption efficiency by the MC method was Li<sup>+</sup> < Mg<sup>2+</sup> ≤ Na<sup>+</sup> < Ca<sup>2+</sup> < K<sup>+</sup> ≤ NH<sub>4</sub><sup>+</sup>.

Changes in the surface structure of Cs-WB were confirmed by SEM after MC treatment (Fig. 3). Taking Fig. 3a as the starting point before the MC treatment, the samples treated with aqueous monovalent cation solutions (Fig. 3c, 3e, 3g, and 3h) did not show the layered structure of clay minerals observed in Cs-WB. The mineral particles were crushed to the extent that particles <0.1 μm in diameter were observed, consistent with the XRD results (Fig. 2). The findings suggest that grinding in the presence of the monovalent ion solution destroys the layered structure effectively. Figures 3b, 3d, and 3f are of samples treated with distilled water or divalent cations. Although the grain size was slightly smaller due to physical pulverization, part of the layered structure characteristic of the clay minerals remained as in Fig. 3a. In the oxalic acid-treated samples (Fig. 3i and 3j), the layered structure, as in Fig. 3a, was observed, but the particle size itself was not refined, and the presence of very sharp-edged particles was confirmed. Previous reports showed that the MC reaction destroys the clay mineral layer (nanosheet surface) and that the destruction and exfoliation of the layer structure progresses further as the milling time increases (Ramadan *et al.*, 2010; Maleki and Karimi-Jashni, 2017). The results of this study suggest that, in the presence of monovalent cations, the layer structure was destroyed and exfoliated, whereas in the presence of water, oxalic acid, and divalent cations, no destruction or exfoliation of the layer structure occurred. Comparing the results (Figs 1 and 2) from MC treatment in the presence of various aqueous solutions revealed that monovalent ions were equally effective at grinding. However, for Cs desorption, NH<sub>4</sub><sup>+</sup>, which is closer to the Cs<sup>+</sup> ion size, was the most effective at promoting ion exchange in the solution, indicating that crushing and ion exchange synergistic effects are essential for Cs desorption.

#### Results of <sup>137</sup>Cs desorption, following MC treatment, from soil collected in Fukushima Prefecture

The previous section proved that MC treatment with ammonium chloride destroyed the layer structure of the clay minerals. As a





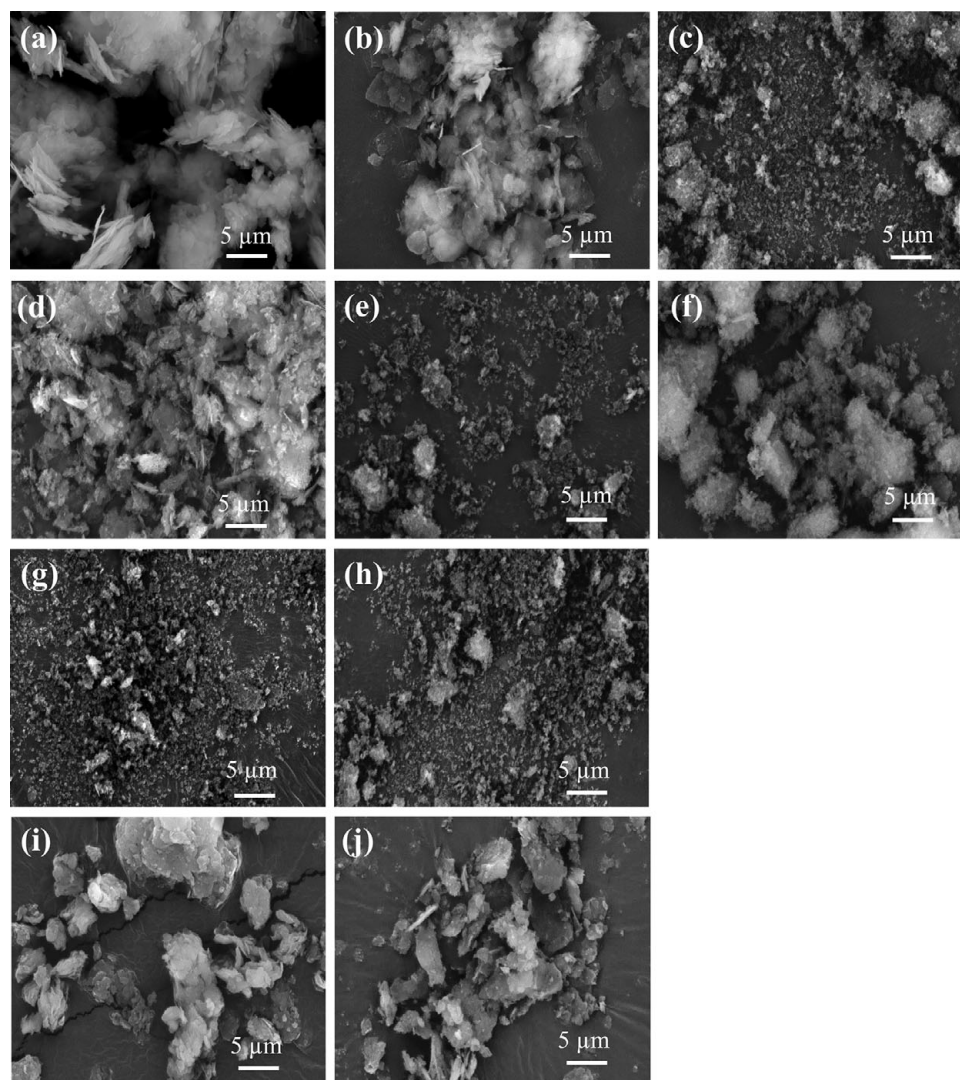
**Figure 2.** XRD patterns before and after mechanochemical treatments: (a) oxalic acid (168 h), (b) oxalic acid (72 h), (c)  $\text{NH}_4\text{Cl}$  (72 h), (d)  $\text{KCl}$  (72 h), (e)  $\text{CaCl}_2$  (72 h), (f)  $\text{NaCl}$  (72 h), (g)  $\text{MgCl}_2$  (72 h), (h)  $\text{LiCl}$  (72 h), (i)  $\text{H}_2\text{O}$  (72 h), and (j) Cs-WB (before treatment). WB = weathered biotite, K = kaolinite. The figure on the left is a close-up of the  $2\theta$  region from 5 to  $13^\circ$   $2\theta$ , magnified  $\times 15$ .

result, MC treatments for desorbing radioactive Cs from soil collected at Fukushima Prefecture were tried. The radioactivity of the soil before treatment was measured; the average concentrations of  $^{137}\text{Cs}$  exceeded the recycling standard ( $8000 \text{ Bq kg}^{-1}$  of soil) by more than 1000 times, being  $\sim 130.2 \text{ kBq kg}^{-1}$  soil in soil A,  $\sim 56.8 \text{ kBq kg}^{-1}$  soil in soil B,  $\sim 42.6 \text{ kBq kg}^{-1}$  soil in soil C, and  $61.0 \text{ kBq kg}^{-1}$  soil in soil D.

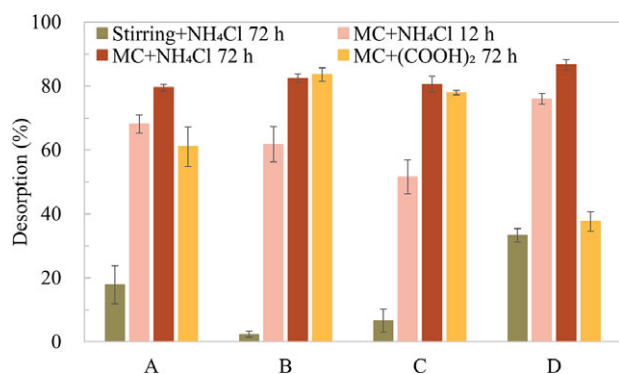
The extent of  $^{137}\text{Cs}$  desorption (Fig. 4) was evaluated for various soils under different conditions. The MC treatment was conducted for 12 h and 72 h with ammonium chloride and 72 h with oxalic acid. Additionally, for comparison, a 72 h slow rotary stirring treatment with ammonium chloride without milling was performed. The results showed that after 72 h of stirring with ammonium chloride without the MC treatment, the extent of desorption varied, ranging from almost no desorption to a maximum of 33% (2.4–33%). The wet chemical treatment with ammonium chloride is a treatment that assumes ion exchange between  $^{137}\text{Cs}^+$  and  $\text{NH}_4^+$  ions adsorbed on the surface of clay minerals, where the ammonium chloride ion can reach. Most of the  $^{137}\text{Cs}$  that was not desorbed should be in the interlayer of clay minerals where radioactive Cs is difficult to ion exchange. When the MC treatment was used, the extent of desorption increased for the ammonium chloride compared with stirring alone; the extent of desorption of the soils treated with ammonium chloride for 12 h were 52–76%, and the extent of desorption of the soils treated for 72 h was 80–87%. However, oxalic acid treatments showed some variation, with the extent of desorption reaching  $\sim 84$  and 78% in some soils, while others had values of 38 and 61%. The degree of desorption in soil sample D was particularly low compared with the other samples. Previous studies investigating the extraction of  $^{137}\text{Cs}$  from Fukushima soil by nitric acid reported that the desorption of  $^{137}\text{Cs}$  varied significantly depending on the type of soil (Parajuli et al., 2016; Yamasaki and Utsunomiya, 2022).

The XRD patterns of soil samples A, B, C, and D (before and after 72 h of oxalic acid, and for 12 and 72 h of ammonium chloride MC treatment) were compared (Fig. 5). The XRD patterns of the various soil samples prior to MC treatment showed stronger quartz reflections than the WB sample, which exhibited only reflections from clay mineral particles. This was due to the use of samples containing particles up to 2 mm in size, including sand and silt. The clay minerals in the soil samples were observed to have 001 reflections at  $6.3^\circ 2\theta$ ,  $8.9^\circ 2\theta$ , and  $12.2^\circ 2\theta$  assigned to vermiculite, a little WB, and kaolinite in sample A. Sample B contained kaolinite and WB. Sample C contained vermiculite, WB, and kaolinite, and sample D contained vermiculite and a small amount of WB.

Additional reflections of calcium–zirconium oxalate hydrate were observed at  $13.1^\circ 2\theta$  and  $15.8^\circ 2\theta$  in soils A, C, and D after MC treatments with oxalic acid. This indicates that the MC treatment caused a reaction between the zirconia in the grinding vessel and balls, the oxalic acid, and the CaO in the soils, resulting in the formation of calcium–zirconium oxalate hydrate. The reason why no peaks appeared in sample B may be due to the small CaO content compared with the other samples (Table 2). In the XRD pattern after 72 h of the MC treatment with oxalic acid, the 001 reflections derived from WB and vermiculite were faintly visible in sample A but disappeared from samples B and C. Sample D had a more minor original 001 reflection but showed residual WB and vermiculite. In other words, the extent of desorption of  $^{137}\text{Cs}$  was consistent with the results of the simulation experiment in the previous section, in which the extent of desorption of  $^{137}\text{Cs}$  was related to the WB. This suggests that an intact micro-portion of WB and vermiculite may eventually serve as a strong adsorption site, considering the report of selective adsorption on WB in Fukushima soil (Mukai et al., 2014) and our SEM observations (Fig. 3) in the previous section.



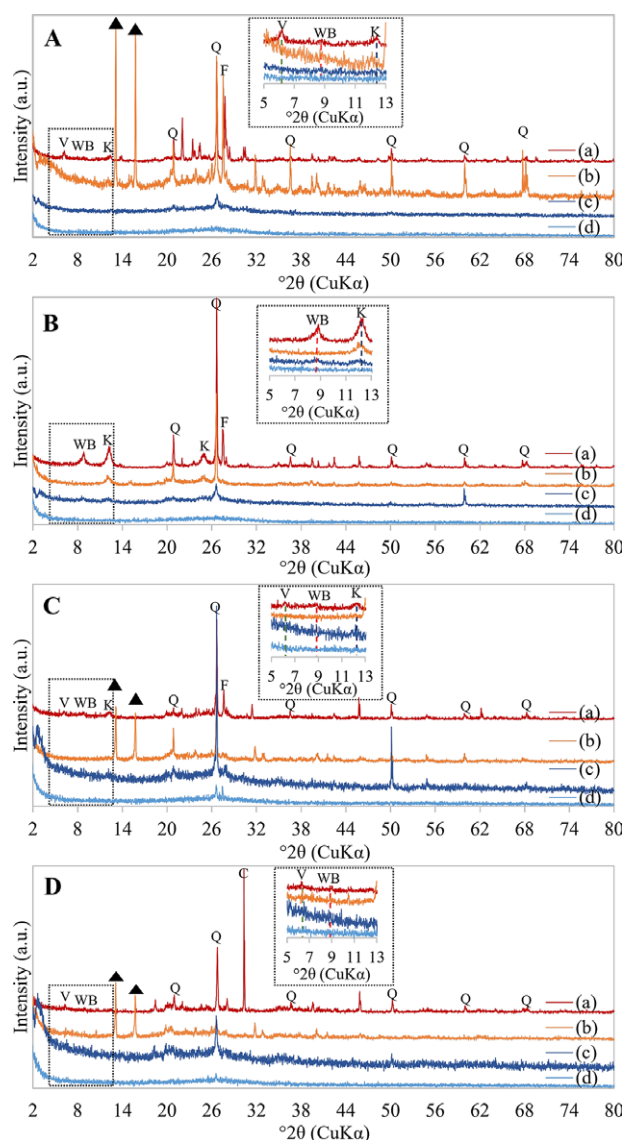
**Figure 3.** SEM images for Cs-WB after MC treatment with various solutions. (a) Cs-WB (before treatment), (b) H<sub>2</sub>O (72 h), (c) LiCl (72 h), (d) MgCl<sub>2</sub> (72 h), (e) NaCl (72 h), (f) CaCl<sub>2</sub> (72 h), (g) KCl (72 h), (h) NH<sub>4</sub>Cl (72 h), (i) oxalic acid (72 h), and (j) oxalic acid (168 h).



**Figure 4.** Desorption of <sup>137</sup>Cs from various soils after 72 h of MC treatment with ammonium chloride or oxalic acid, and after 12 h of the MC treatment with ammonium chloride and 72 h of slow rotating stirring. Error bars equate to standard deviation data for three replicate results.

Comparing the XRD patterns (Fig. 5) after 12 and 72 h of MC treatment with ammonium chloride, the WB peaks were faintly visible in soils A, B, C, and D after 12 h of treatment, and vermiculite

peaks in soil D, but the peaks disappeared after 72 h. Previous studies (Baki *et al.*, 2022; Da *et al.*, 2022; Ku Ishak *et al.*, 2022) reported that mica ground in a planetary mill undergoes destruction and exfoliation of its layered structure. Based on this finding, the 72 h treatment may have caused exfoliation of the layered structure of WB and vermiculite. The result suggests that the 12 h treatment destroyed the adsorption sites near the surface layer of the clay minerals, and the 72 h treatment further affected the internal sites. Considering that ball milling gradually removes Cs adsorption sites from the edges of the material, <sup>137</sup>Cs was probably adsorbed not only at specific sites such as FES but also at deeper interlayer core sites than the edge sites. The differences in desorption behavior between ammonium chloride treatment and oxalic acid treatment was evident from SEM observations (Fig. 3), which showed no destruction or exfoliation of the layer structure by oxalic acid, preventing the removal of <sup>137</sup>Cs adsorbed in the interlayer core sites. In contrast, ammonium chloride disrupted and exfoliated the clay mineral layer structure effectively, transforming interlayer <sup>137</sup>Cs from a closed state to a surface-adsorbed state accessible to chemical treatment. However, some <sup>137</sup>Cs is inferred to remain adsorbed on the delaminated surface even after this process.



**Figure 5.** XRD patterns before and after MC treatment in soil samples A, B, C, and D: (A) soil before MC treatment; (B) after MC treatment with oxalic acid for 72 h; (C) after MC treatment with ammonium chloride for 12 h; and (D) after MC treatment with ammonium chloride for 72 h. V = vermiculite, K = kaolinite, WB = weathered biotite, Q = quartz, F = feldspar, C = calcite; ▲ denotes Calcium-zirconium oxalate hydrate. The inset is a close-up of the region from 5 to 13°2θ.

Based on the results above, MC treatment using ammonium chloride desorbs effectively trace amounts of radioactive Cs which are strongly adsorbed on the edges and core sites of the clay minerals due to the synergistic effect of physical treatments, such as exfoliation and pulverization of the layered structure of clay minerals, and chemical interaction by ion exchange.

## Conclusions

The desorption behavior of Cs adsorbed onto weathered biotite, which occurs abundantly in the soil of Fukushima Prefecture, was investigated using mechanochemical treatment, which combines physical grinding and wet processing. The effectiveness of this method for desorbing radioactive Cs from real contaminated soil was confirmed. XRD analysis and SEM observations confirmed that the MC treatment promoted the pulverization of clay

minerals, and the presence of monovalent cations during the MC treatment promoted the destruction of the layered structure of WB through exfoliation. The exfoliation and pulverization probably promoted access by chemical reagents to the Cs adsorption sites and improved desorption. In particular, treatment with ammonium chloride was effective at desorbing both stable and radioactive Cs from WB.

The application of the MC method, including ball milling, to soil increased the desorption of  $^{137}\text{Cs}$  due to a more broken clay mineral structure, indicating that radioactive Cs penetrates not only to the surface or frayed edges but also deep into the clay mineral interlayers. The MC method in the presence of ammonium chloride solution is a simple method that can desorb radioactive Cs adsorbed on the interlayer of clay minerals in the contaminated soil, demonstrating its applicability to layered silicate clay minerals such as mica. In particular, this method shows great promise as a post-treatment option for fine-grained soil separated through classification processes in complex environmental samples, such as Fukushima Prefecture soil (Parajuli et al., 2016; Koarashi et al., 2019).

The MC treatment method proposed here is suggested for decontaminating radioactive soils contaminated with Cs, and the secondary effluent and residual soil generated after treatment must be managed appropriately and solidified (Hara et al., 2022; Sato et al., 2022) according to laws and standards, and then disposed of as final waste. However, if the levels are below the regulatory threshold, recycling of the soil may be possible. The approach is expected to reduce the final disposal volume of the removed soil significantly, leading to a reduction in the required disposal space and the associated management costs.

**Data availability statement.** Data are available from corresponding author upon reasonable request.

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## References

- Akemoto, Y., Iwamura, T., Takahashi, S., Kan, M., & Tanaka, S. (2021). Desorption of  $\text{Cs}^+$  from contaminated biotite with a low molecular mass organic acid. *Journal of Environmental Chemical Engineering*, 9, 106101.
- Baki, V.A., Ke, X., Heath, A., Calabria-Holley, J., Terzi, C., & Sirin, M. (2022). The impact of mechanochemical activation on the physicochemical properties and pozzolanic reactivity of kaolinite, muscovite and montmorillonite. *Cement and Concrete Research*, 162, 106962.
- Bradbury, M.H., & Baeyens, B. (2000). A generalised sorption model for the concentration dependent uptake of caesium by argillaceous rocks. *Journal of Contaminant Hydrology*, 42, 141–163.



- Cornell, R.M. (1993). Adsorption of cesium on minerals: a review. *Journal of Radioanalytical and Nuclear Chemistry*, 171, 483–500.
- Da, Y., Liu, J., Gao, Z., & Xue, X. (2022). Studying the influence of mica particle size on the properties of epoxy acrylate/mica composite coatings through reducing mica particle size by the ball-milled method. *Coatings*, 12, 98.
- Frost, R.L., Makó, É., Kristóf, J., Horváth, E., & Klopogge, J.T. (2001). Mechanochemical treatment of kaolinite. *Journal of Colloid and Interface Science*, 239, 458–466.
- Hara, T., Nakase, M., Harigai, M., & Takeshita, K. (2022). Recovery and immobilization of cesium from aqueous solution after hydrothermal treatment using functional porous glass. *Journal of Nuclear Science and Technology*, 59, 1304–1313.
- Jackson, M.L. (1962). Interlayering of expansive layer silicates in soils by chemical weathering. *Clays and Clay Minerals*, 11, 29–46.
- Japan Atomic Energy Agency (2017). Airborne Monitoring in the Distribution Survey of Radioactive Substances (FY 2011 - FY 2017 The Ministry of Education, Culture, Sports, Science and Technology, the U.S. Department of Energy, and the Secretariat of the Nuclear Regulation Authority). *Database for Radioactive Substance Monitoring Data*. <[https://emdb.jaea.go.jp/emdb\\_old/en/portals/b1010301/](https://emdb.jaea.go.jp/emdb_old/en/portals/b1010301/)> (7 September 2023).
- Kikuchi, R., Mukai, H., Kuramata, C., & Kogure, T. (2015). Cs-sorption in weathered biotite from Fukushima granitic soil. *Journal of Mineralogical and Petrological Sciences*, 110, 126–134.
- Koarashi, J., Nishimura, S., Atarashi-Andoh, M., Muto, K., & Matsunaga, T. (2019). A new perspective on the  $^{137}\text{Cs}$  retention mechanism in surface soils during the early stage after the Fukushima nuclear accident. *Scientific Reports*, 9, 7034.
- Ku Ishak, K.E.H., Saad, S., Saiyid Hashim, S.F., & Hussin, H. (2022). Statistical analysis of dry grinding of mica in planetary mill. *Pertanika Journal of Science and Technology*, 30, 2191–2204.
- Lee, J., Park, S.-M., Jeon, E.-K., & Baek, K. (2017). Selective and irreversible adsorption mechanism of cesium on illite. *Applied Geochemistry*, 85, 188–193.
- Maleki, S., & Karimi-Jashni, A. (2017). Effect of ball milling process on the structure of local clay and its adsorption performance for Ni(II) removal. *Applied Clay Science*, 137, 213–224.
- McKinley, J.P., Zeissler, C.J., Zachara, J.M., Serne, R.J., Lindstrom, R.M., Schaef, H.T., & Orr, R.D. (2001). Distribution and retention of  $^{137}\text{Cs}$  in sediments at the Hanford Site, Washington. *Environmental Science & Technology*, 35, 3433–3441.
- McKinley, J.P., Zachara, J.M., Heald, S.M., Dohnalkova, A., Newville, M.G., & Sutton, S.R. (2004). Microscale distribution of cesium sorbed to biotite and muscovite. *Environmental Science & Technology*, 38, 1017–1023.
- Ministry of the Environment of Japan (2019a). Strategy for developing technology for volume reduction and recycling of removed soil at interim storage facility – review to achieve strategic goals (in Japanese). <[http://josen.env.go.jp/chukanchozou/facility/effort/investigative\\_commission/pdf/investigative\\_commission\\_review\\_1903.pdf?1904](http://josen.env.go.jp/chukanchozou/facility/effort/investigative_commission/pdf/investigative_commission_review_1903.pdf?1904)> (accessed 17 April 2023).
- Ministry of the Environment of Japan (2019b). Basic Concept for Safe Use of Removed Soil Processed into Recycled Materials [MOE]. *BOOKLET to Provide Basic Information Regarding Health Effects of Radiation* (4th edn). <<https://www.env.go.jp/en/chemi/rhm/basic-info/1st/09-02-05.html>> (accessed 30 January 2025).
- Moldoveanu, G.A., & Papangelakis, V.G. (2012). Recovery of rare earth elements adsorbed on clay minerals: I. Desorption mechanism. *Hydrometallurgy*, 117–118, 71–78.
- Motokawa, R., Endo, H., Yokoyama, S., Nishitsuji, S., Kobayashi, T., Szuki, S., and Yaita, T. (2014a). Collective structural changes in vermiculite clay suspensions induced by cesium ions. *Scientific Reports*, 4, 6585\_1–6585\_6.
- Motokawa, R., Endo, H., Yokoyama, S., Ogawa, H., Kobayashi, T., Suzuki, S., & Yaita, T. (2014b). Mesoscopic structures of vermiculite and weathered biotite clays in suspension with and without cesium ions. *Langmuir*, 30, 15127–15134.
- Mukai, H., Hatta, T., Kitazawa, H., Yamada, H., Yaita, T., & Kogure, T. (2014). Speciation of radioactive soil particles in the Fukushima contaminated area by IP autoradiography and microanalyses. *Environmental Science & Technology*, 48, 13053–13059.
- Mukai, H., Motai, S., Yaita, T., & Kogure, T. (2016). Identification of the actual cesium-adsorbing materials in the contaminated Fukushima soil. *Applied Clay Science*, 121–122, 188–193.
- Murota, K., Tanoi, K., Ochiai, A., Utsunomiya, S., & Saito, T. (2020). Desorption mechanisms of cesium from illite and vermiculite. *Applied Geochemistry*, 123, 104768.
- Nakao, A., Thiry, Y., Funakawa, S., & Kosaki, T. (2008). Characterization of the frayed edge site of micaceous minerals in soil clays influenced by different pedogenetic conditions in Japan and northern Thailand. *Soil Science & Plant Nutrition*, 54, 479–489.
- Papirer, E., Eckhardt, A., Muller, F., & Yvon, J. (1990). Grinding of muscovite: influence of the grinding medium. *Journal of Materials Science*, 25, 5109–5117.
- Parajuli, D., Suzuki, Y., Sato, M., Takahashi, A., Tanaka, H., & Kawamoto, T. (2016). Assessment of the measures for the extraction or fixation of radiocesium in soil. *Geoderma*, 267, 169–173.
- Park, S.-M., Alessi, D.S., & Baek, K. (2019). Selective adsorption and irreversible fixation behavior of cesium onto 2:1 layered clay mineral: a mini review. *Journal of Hazardous Materials*, 369, 569–576.
- Ramadan, A.R., Esawi, A.M.K., & Gawad, A.A. (2010). Effect of ball milling on the structure of  $\text{Na}^+$ -montmorillonite and organo-montmorillonite (Cloisite 30B). *Applied Clay Science*, 47, 196–202.
- Sato, T., Oya, Y., Raudhatul Islam, C., Kuroda, K., Nakabayashi, R., Kudo, I., Kato, K., & Taniguchi, M. (2022). Applicability of geopolymers as a solidification matrix for wastes containing radioactive cesium. *Material Cycles and Waste Management Research*, 33, 448–455.
- Sawhney, B.L. (1972). Selective sorption and fixation of cations by clay minerals: a review. *Clays and Clay Minerals*, 20, 93–100.
- Xia, M., Jiang, Y., Zhao, L., Li, F., Xue, B., Sun, M., Liu, D., & Zhang, X. (2010). Wet grinding of montmorillonite and its effect on the properties of mesoporous montmorillonite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 356, 1–9.
- Yaita, T., Matsumura, D., Kobayashi, T., Suzuki, S., Tsuji, T., Okumura, M., Machida, M., Motokawa, R., Mukai, H., & Kogure, T. (2016). Investigation of cesium sorption mechanisms into clay minerals. *Global Environmental Research*, 20, 033–044.
- Yamasaki, S., & Utsunomiya, S. (2022). A review of efforts for volume reduction of contaminated soil in the ten years after the accident at the Fukushima Daiichi Nuclear Power Plant. *Journal of Nuclear Science and Technology*, 59, 135–147.