Behaviors of Desorption Agents During Removal of Cs From Clay Minerals and Actual Soil

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The behaviors of various desorption agents were investigated during the desorption of cesium (Cs) from samples of clay minerals and actual soil. Results showed that polymeric cation exchange agents (polyethyleneimine (PEI)) efficiently desorbed Cs from expandable montmorillonite, whereas acidic desorption solutions containing HCl or PEI removed considerable Cs from hydrobiotite. However, most desorption agents could desorb only 54% of Cs from illite because of Cs's specific adsorption to selective adsorption sites. Cs desorption from an actual soil sample containing Cs-selective clay mineral illite (< 200 μm) and extracted from near South Korea's Kori Nuclear Power Plant was also investigated. Considerable adsorbed ^{137}Cs was expected to be located at Cs-selective sites when the ^{137}Cs loading was much lower than the sample's cation exchange capacity. At this low ^{137}Cs loading, the total Cs amount desorbed by repeated washing varied by desorption agent in the order HCl > PEI > NH$_4^+$, and the highest Cs desorption amount achieved using HCl was 83%. Unlike other desorption agents with only cation exchange capabilities, HCl can attack minerals and induce dissolution of metallic elements. HCl's ability to both alter minerals and induce H$^+$/Cs$^+$ ion exchange is expected to promote Cs desorption from actual soil samples.

Keywords: Cesium, Soil, Clay, Desorption, Washing

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1. Introduction

Inadvertent and accidental release of radiocesium from nuclear facilities into the environment produces problematic Cs-contaminated soil wastes [1, 2]. Among various soil components, the 2:1 clay minerals strongly and specifically bind radiocesium [3, 4], and thus remediation of Cs-contaminated soil generally faces technical challenges.

A variety of clay minerals (including such as kaolinite, illite, smectite, and vermiculite), can be present in soil depending on parent minerals and weathering conditions. Each type of clay mineral has distinguishable mineralogical characteristics including expansion properties and cation exchange capacity (CEC), among many others [5]. Consequently, individual clay minerals display different Cs adsorption and desorption behaviors [3, 6, 7]. For example, Cs adsorption on kaolinite (1:1 clay mineral) mainly takes place on the external surface of a particle through formation of an outer-sphere complex. Moreover, the Cs adsorbed to kaolinite is readily exchangeable [8, 9].

On the other hand, 2:1 clay minerals contain additional Cs adsorption sites, such as hydrated or dehydrated interlayer sites, as well as frayed edge sites (FES), in addition to the external planar sites [7]. In particular, FES can be formed as a result of weathering at the edges of potassium-bearing micaceous clay minerals. It has been experimentally and theoretically proven that the highly Cs-selective FES can adsorb Cs in stable form [10-13], and that the bound Cs is stabilized by consequent shrinkage of the weathered interlayers [14-16]. For this reason, the adsorbed Cs ions on non-expandable illite, and on micas containing FES, are hardly removable [17, 18]. On the other hand, highly expandable montmorillonite has Cs adsorption sites in negatively charged interlayers. Moreover, it was reported that a small fraction of Cs could be adsorbed via strong inner-sphere complexations on the mineral when the Cs loading was low [19, 20]. Meanwhile, partially expandable vermiculite interlayers sometimes undergo dehydration and shrinkage after Cs adsorption, and the desorption of such

stabilized Cs has been reported to be inefficient [5].

Various attempts have been made to desorb Cs from clay minerals using organic and inorganic cations based on ion-exchange reactions between cations and Cs [21]. Even though the excess Mg^{2+} ions could extract significant (~90%) amounts of Cs from vermiculite, Cs removal by ammonium or metal ions from montmorillonite and illite were relatively inefficient (50–60%) [22, 23]. It was also reported that the highest achievable Cs desorption from illite by NH_4^+ (1 M) was only 54%, even after 8 weeks of reaction [18]. In contrast, cationic surfactant and polymers have been reported to be efficient Cs desorption agents for fully and partially expandable clay minerals such as montmorillonite (~95%, ^{137}Cs) and hydrobiotite (~87%, ^{133}Cs). The expansion of interlayers induced by polymer or surfactant intercalation in the interlayers enhanced ion-exchange reactions between cations and Cs [16, 20, 24, 25]. Meanwhile, a hydrogen peroxide solution promoted expansion of the interlayers of hydrobiotite, which is a mixed-layer clay mineral of expandable vermiculite and non-expandable mica. Moreover, hydrogen peroxide also potentiated the ion-exchange capability when a complementary cation exchange agent (Mg^{2+}) was added with the Cs [26].

Organic and inorganic acids have also been investigated as Cs desorption agents. The acids are capable of dissolving mineral components and elements, and thus desorption of Cs can be enhanced with the help of the H^+/Cs^+ exchange reaction [27-30]. Even though various acids have shown promising Cs-desorption performance against single clay minerals, the reported Cs-desorption efficiency of oxalate from the actual soil was less than 63%, even after the 68-day treatment [31].

Although various Cs-desorption agents have been investigated for use against single clay minerals, comparisons of the effectiveness of Cs-desorption agents against different kinds of clay minerals are also important subjects to investigate. Moreover, the trend of Cs desorption from actual soil samples is frequently different from that involving single clay minerals. For this reason, the Cs desorption

properties of the agents must be evaluated by considering the mineral components in the actual soil.

In the work reported in this paper, we investigated the behavior of various desorption agents (including polymeric cation exchange agents, single molecular cations, and acid) for desorption of Cs from clay minerals and actual soil samples. The clay minerals investigated included expandable montmorillonite, non-expandable illite, and mixed-layer clay of expandable vermiculite and non-expandable biotite (hydrobiotite). To investigate the behavior of Cs-desorption from actual soil samples containing various soil constituents, soil samples were collected from near the Kori Nuclear Power Plant (NPP). In addition, the correlations between the mineral components and Cs-desorption behaviors were investigated.

2. Experimental

2.1 Materials

Montmorillonite (MT, SAz-1 from The Clay Minerals Society, USA) and illite (IL, 2,500 mesh, Youngkoong Illite Co., Ltd.) were used as received. A hydrobiotite (HB, < 38 μm) sample was prepared by sequential treatment of vermiculite (Sigam-Aldrich) by mechanical milling (M 20 universal mill, IKA) and mechanical sieving using a standard test sieve (400 mesh) [16].

Cesium chloride, tetramethyl ammonium chloride (TMA), hydrochloric acid, poly(diallyldimethylammonium chloride) (PDDA, Mw < 100 kDa), hydrochloric acid, ammonium nitrate, and poly(ethyleneimine) with Mw = ~2 kDa (PEI_{2k}) and ~25 kDa (PEI_{25k}), were purchased from Sigma-Aldrich and used as received.

2.2 Sampling and fractionation of soil

The soil samples were taken at depths of 0 to 15 cm from the soil surface within 2 km of the Kori NPP (35° 20′ 33″ N, 129° 17′ 33″ E). The soil fraction under 200 μm (SF200) was obtained by dry-sieving the soil using a vibratory sieve shaker (Retsch AS 200) with a standard sieve (Retsch, ISO 3310/1). The soil weight fraction < 200 μm was 36.5%.

2.3 Characterization of clay minerals and soil samples

The compositions of the clay minerals and SF200 were determined by X-ray diffraction (XRD) analysis using a Rigaku SmartLab diffractometer (Japan). The elemental contents in the samples were determined by energy dispersive X-ray fluorescence (XRF) spectrometry analysis using an S2 RANGER (Bruker). For the XRF analysis, a double-layer pellet (sample and boric acid) was prepared by pressing the clay or soil (200 mg) on an as-prepared boric acid pellet (6 g) using a hydraulic press at 20 t [20]. The cation exchange capacity (CEC) of clay minerals and soil samples were determined by following the SW-846 Test Method 9081 (U.S. Environmental Protection Agency).

2.4 Preparation of Cs-adsorbed clay minerals and soil samples

A portion (35 g) of each sample (MT, IL, HB, and SF200) was mixed with 3 mM CsCl solution in deionized water (350 mL). Then, the Cs adsorption was allowed to reach equilibration by shaking the mixture for 7 days at 25°C in a shaking incubator. The Cs-adsorbed clay minerals and SF200 sample were collected by centrifugation, followed by washing with deionized water. To estimate the amounts of adsorbed Cs on the clay minerals and SF200, unbound Cs in the liquid was quantified using inductively coupled plasma mass spectroscopy (ICP-MS, ELAN DRC II, PerkinElmer, USA). The aqueous phase was filtered using a polyvinylidene fluoride (PVDF) syringe filter (pore size = 0.2 μm) prior to the measurements. The Cs-adsorbed MT, IL, HB, and SF200 samples were denoted as Cs-MT, Cs-IL, Cs-HB, and Cs-SF200, respectively.

2.5 Desorption of Cs from clay minerals and soil samples

The Cs-adsorbed clay minerals and SF200 (300 mg) were each mixed with (30 mL) solutions containing various desorption agents (PEI$_{2k}$, PEI$_{25k}$, TMA, PDDA, HCl, or NH$_4^+$), and the concentration of desorption agent was 20 mmol per gram of clay minerals or SF200. In the cases of the PEI$_{2k}$, PEI$_{25k}$, and NH$_4^+$ solutions, the solution pH was adjusted to pH 3 using 1 M HCl solution [32]. The mixture was placed in a horizontal shaker for 1 day at 20°C or 80°C. The clay minerals and soil samples were removed by centrifugation, and supernatants were filtered with an Amicon Ultra centrifugal filter (Millipore, molecular weight cut-off (MWCO) = 10 kDa). The total amount of desorbed Cs in the supernatant was quantified by ICP-MS.

2.6 Adsorption and desorption of radiocesium

The SF200 (35 g) was added to a ^{137}Cs solution (68.8 Bq·mL^{-1}, 175 mL) and the resulting mixture was shaken at 25°C for 7 days. The ^{137}Cs-adsorbed SF200 (^{137}Cs-SF200) was separated from aqueous phase by centrifugation for 1 hr. The ^{137}Cs-SF200 was air-dried at room temperature, and the aqueous phase was filtered using a PVDF syringe filter (pore size = 0.2 μm). The radioactivity of the filtrate (C, Bq·mL^{-1}) and the dried ^{137}Cs-SF200 (q, Bq·mL^{-1}) were measured using a high-purity germanium detector (HPGe) equipped with a multi-channel analyzer (MCA, CANBERRA Ind.). The minimum detectable activity was maintained below 0.02 Bq·g^{-1}. The radiocesium distribution coefficient (K_d) of the SF200 was calculated using.

$$K_d = q/C \qquad (1)$$

The desorption of radiocesium from the ^{137}Cs-SF200 (300 mg) was carried out by following the experimental method described above. Solutions (30 mL) containing 20 mmol·g^{-1} soil were mixed with desorption agents (PEI$_{2k}$, PEI$_{25k}$, TMA, PDDA, HCl, or NH$_4^+$) at 20°C for 1 day. For repeated radiocesium desorption experiments, the ^{137}Cs-SF200 (300 mg) was reacted with solutions (30 mL) containing 20 or 50 mmol·g^{-1} soil of PEI$_{2k}$, HCl, or NH$_4^+$ at 20°C for 1 day. Then, the aqueous phase was replaced with a fresh solution containing the desorption agent every 24 hr, after separating the solids by centrifugation. The radioactivity of the liquid phase was determined using a HPGe equipped with a MCA. This was done after filtration using an Amicon Ultra centrifugal filter (MWCO = 10 kDa).

3. Results and discussion

3.1 Characterization of clay minerals and soil samples

XRD analysis of the clay minerals and SF200 was carried out to identify minerals present in the samples (Fig. 1). Each clay mineral sample showed its own typical XRD pattern [5], and characteristic peaks of montmorillonite and illite were observed at $2\theta = {\sim}6.1°$ and ~8.8°, respectively. The HB sample showed an XRD pattern of a mixed-layer clay mineral containing expandable vermiculite and non-expandable mica. The peak characteristic of hydrobiotite was observed at $2\theta = 7.4°$, and peaks of mica and vermiculite were also observed at $2\theta = 8.8°$ and 6.1° [16]. From the XRD pattern of the SF200, illite and kaolinite peaks were found at $2\theta = {\sim}8.8°$ and ~12°, respectively, and strong peaks characteristics of quartz were also observed at $2\theta = {\sim}21.2°$ and ~26.3° [33, 34]. Finally, it was determined that the SF200 contains quartz as well as clay minerals that included illite and kaolinite.

For analysis of the elemental contents in the samples, XRF measurements of the clay minerals and the SF200 were carried out (Table 1). As expected, the element contained in nearly all the samples was Si because it is a major component of phyllosilicate clay minerals and quartz. The mineral montmorillonite (SAz-1), which contains Ca

Table 1. Elemental compositions of the clay minerals and the soil sample

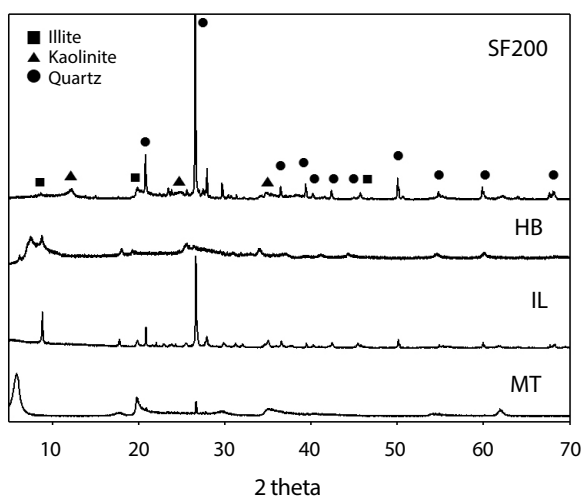| Sample	Elemental composition (%)							
	SiO_2	Al_2O_3	CaO	Na_2O	MgO	K_2O	TiO_2	Fe_2O_3
MT	59.4	15.0	6.8	2.9	4.6	0.20	0.2	3.3
IL	60.8	23.5	0.1	1.5	0.3	5.90	0.4	3.7
HB	39.2	9.9	2.2	0.1	23.9	6.31	1.3	9.8
SF200	60.5	27.9	0.3	1.0	2.1	2.70	0.5	4.6

Fig. 1. XRD patterns of montmorillonite (MT), illite (IL), and hydrobiotite (HB); and the fraction of an actual soil sample (< 200 μm).

Table 2. Amount of Cs adsorbed on the clay minerals and SF200[1], and percentage of adsorbed Cs ions to CEC of the samples

Samples	Adsorbed Cs (μmol·g⁻¹)	CEC[2] (meq·g⁻¹)	Cs/CEC (%)
Cs-MT	29.6	1.33	2.2
Cs-IL	22.4	0.19	11.5
Cs-HB	28.8	0.99	2.9
CS-SF200	26.5	0.28	9.3

*Initial Cs/solid ratio = 30 μmol·g⁻¹
**The CEC values of pristine samples

3.2 Desorption of Cs from clay minerals and soil sample

The Cs-adsorbed clay minerals and the soil sample were prepared by reacting the samples with [133]CsCl solutions for 7 days, and the initial Cs/solid ratio was 30 μmol·g⁻¹ (Table 2). Because each clay mineral and soil sample has a different CEC value, the fraction of adsorbed Cs to total CEC varied from 2.2% (Cs-MT) to 11.5% (Cs-IL). In the case of Cs-SF200, the adsorbed amount of Cs was 26.5 μmol·g⁻¹ of Cs, equivalent to 9.3% of CEC.

The efficiency of Cs desorption from clay minerals and soil samples by various desorption agents was analyzed. Polymeric cations (PEI_{2k}, PEI_{25k}, and PDDA), single molecular cations (TMA and NH_4^+), and strong acid (HCl) were tested as desorption agents. The PDDA and TMA contain permanently charged quaternary ammonium cations.
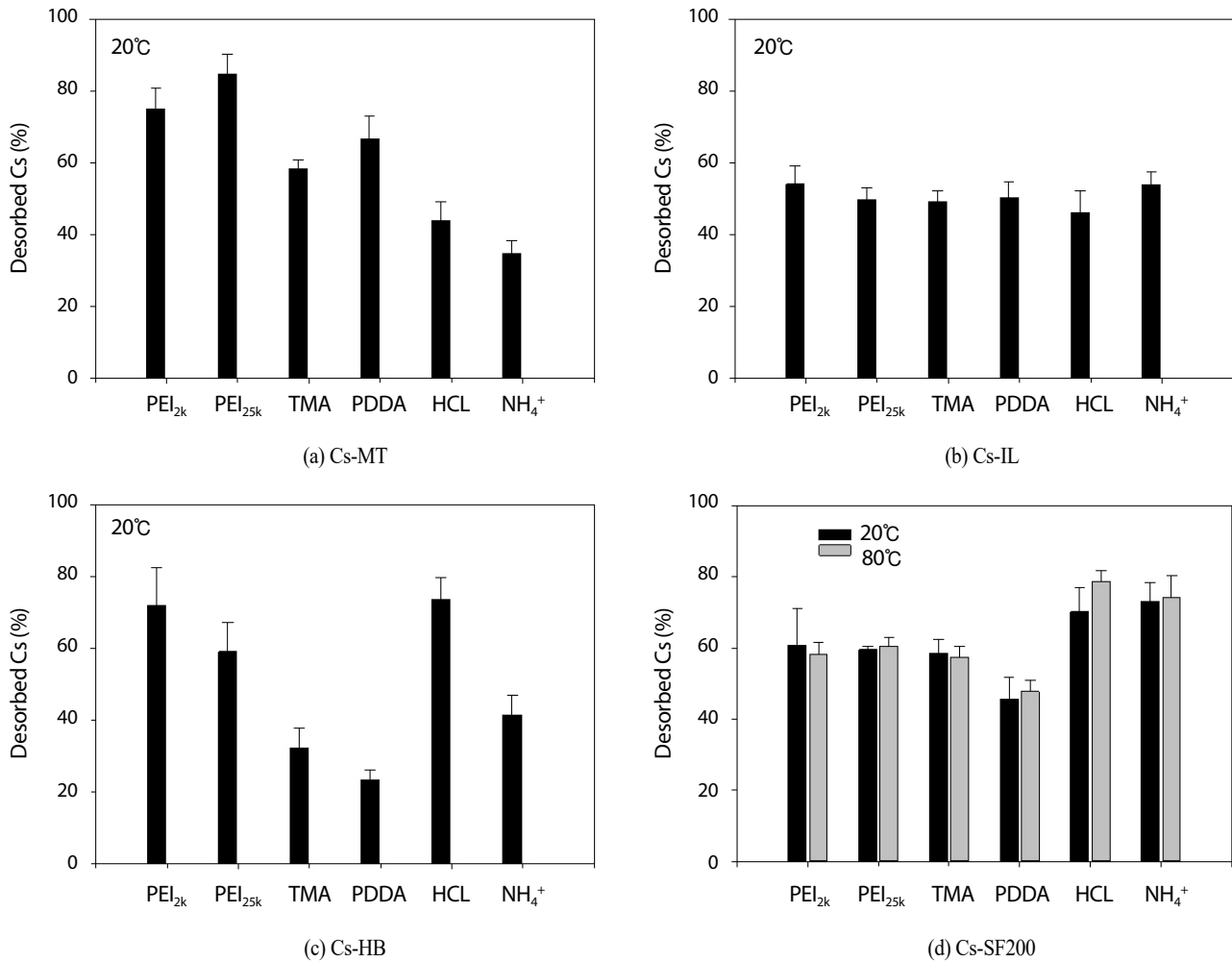
as an exchangeable interlayer cation, showed high Ca content (CaO = 6.8%). Similarly, the IL sample showed high K content (K_2O = 5.9%) because its interlayer cation is K. In the case of HB, which is composed of mixed layers of vermiculite and biotite, both Mg and K were abundant in the sample because they are interlayer cations of vermiculite and biotite, respectively. Because trioctahedral layers of biotite is composed of Mg and Fe, the HB sample also showed high Fe content. The SF200 sample contained relatively high amounts of K compared to other available interlayer cations, such as Na or Ca. This supports the presence of micaceous clay minerals, such as illite, in the SF200 sample.

Fig. 2. Cs-desorption efficiency of various desorption agents (20 mmol·g^{-1}) against (a) Cs-MT, (b) Cs-IL, (c) Cs-HB, and (d) Cs-SF200 (24 hr reaction).

In contrast, PEI and ammonium nitrate can have different protonation states depending on the pH of solutions [16, 32]; thus, the pH of those solutions were maintained at pH 3. Even though both TMA and NH$_4^+$ are single molecular cations, TMA has a slightly bulkier structure compared to NH$_4^+$ because of the four methyl groups in TMA. Unlike the other desorption agents, which have only ion-exchange ability, HCl is not only able to decompose mineral structures and to dissolve metallic elements from clay minerals but also can induce ion-exchange with Cs [28, 35, 36]. The added amount of desorption agents was 20 mmol·g^{-1} based on the cations contained in the desorption agents. This

amount is at least ~7 times higher than the amount of Cs adsorbed on the clay minerals and soil samples.

Fig. 2(a) shows the amount of Cs desorbed from the Cs-MT. The large molecular polymeric cations (such as PEI and PDDA) showed higher Cs desorption efficiency compared to smaller molecular cations such as TMA, H$^+$, or NH$_4^+$. The amount of Cs desorbed by PEI$_{25k}$ solution at pH 3 was $84.7 \pm 5.5\%$ while that achieved by NH$_4^+$ solution at pH 3 was only $34.7 \pm 3.5\%$. It was reported that the cationic polymers can be intercalated into the interlayers of montmorillonite, and that this results in expansion of the interlayers [15]. Once the cation polymer is adsorbed to

the interlayers, the locally increased cation concentration enhances desorption of Cs from the montmorillonite [15]. Although both TMA and PDDA contain permanently charged quaternary ammonium ions, the polymeric PDDA showed better Cs desorption than monomolecular TMA did. This indicates the beneficial effect of a polymeric desorption agent for Cs desorption from montmorillonite.

In the case of Cs-IL, the tested desorption agents showed similar Cs removal efficiencies (less than ~54%, Fig. 2(b)). It is well known that illitic clay minerals possess highly Cs-selective adsorption sites, such as FES and Type II sites [11]. Thus, the Cs ions adsorbed to such adsorption sites are hardly exchangeable with cations [17, 18]. The content of the most Cs-selective Type I sites (FES) and the second highest Cs-selective Type II sites in illite are generally less than 0.25% and 20% of the CEC, respectively [11]. Based on our experimental results, it is expected that the adsorption sites that correspond to ~5.3% of the CEC can strongly bind Cs ions, and such Cs ions are not readily exchangeable with any desorption agents.

In the case of Cs-HB, the amount of Cs desorbed by both HCl and PEI_{2k} (pH 3) solutions was ~73% (Fig. 2(c)). Moreover, the acidic solution containing PEI_{25k} and NH_4^+ at pH 3 also showed higher Cs removal efficiency than did quaternary ammonium ions dissolved in deionized water (PDDA = 23%). Similar to these results, it was previously reported that Cs desorption from hydrobiotite by PEI or NH_4^+ increased as the solution pH was decreased, and only pH adjustment of the hydrobiotite dispersion to pH 3 could induce ~30% of Cs desorption [16]. In this regard, it is predicted that acidic solutions could potentiate desorption of Cs from hydrobiotite.

Finally, the Cs removal capabilities of the desorption agents against Cs-SF200 were observed. At 20°C, the average Cs desorption efficiency of NH_4^+ and HCl was 73% and 70%, respectively, and these desorption agents showed slightly higher Cs desorption efficiencies than the other desorption agents did (50–60%). The amount of desorbed Cs at higher temperature (80°C) was similar to that obtained at
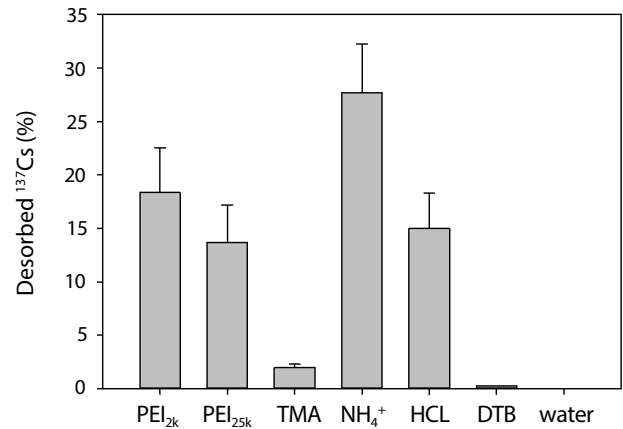

Fig. 3. Amount of radiocesium desorbed from ^{137}Cs-SF200 after reaction with various desorption agents (20 mmol·g^{-1}) at 20°C for 24 hr.

20°C. However, the Cs desorption efficiency of HCl was increased by ~9% after raising the temperature from 20°C to 80°C, and the highest Cs desorption from Cs-SF200 (79%) was achieved using HCl solution at 80°C. Unlike clay mineral samples, the actual soil fraction sample (Cs-SF200) contained various soil components such as primary minerals, clay minerals, and soil organic materials. More specifically, SF200 contained quartz, illite, and kaolinite. The content of Cs-selective FES sites in illite is generally less than 0.25% of the CEC [11, 37, 38], and the illite content in the SF200 sample was also expected to be low. Because the amount of Cs adsorbed on Cs-SF200 was 9.3% of the CEC (Table 2), it was predicted that most of the adsorbed Cs ions would be present at non-selective adsorption sites.

3.3 Desorption of ^{137}Cs from the soil samples

The adsorption of ^{137}Cs on the actual soil sample (SF200) was analyzed. After equilibration of the adsorption reaction, the measured radioactivity of ^{137}Cs-SF200 was 343.45 Bq·g^{-1}, and the calculated Cs distribution coefficient (K_d) of SF200 was 4347 mL·g^{-1}. This adsorbed amount of ^{137}Cs was equivalent to 0.78 pmol·g^{-1}, and only 2.8×10^{-7}% of CEC was occupied by the adsorbed ^{137}Cs. In low-concentration ^{137}Cs solutions, Cs ions tend to be sequestered by
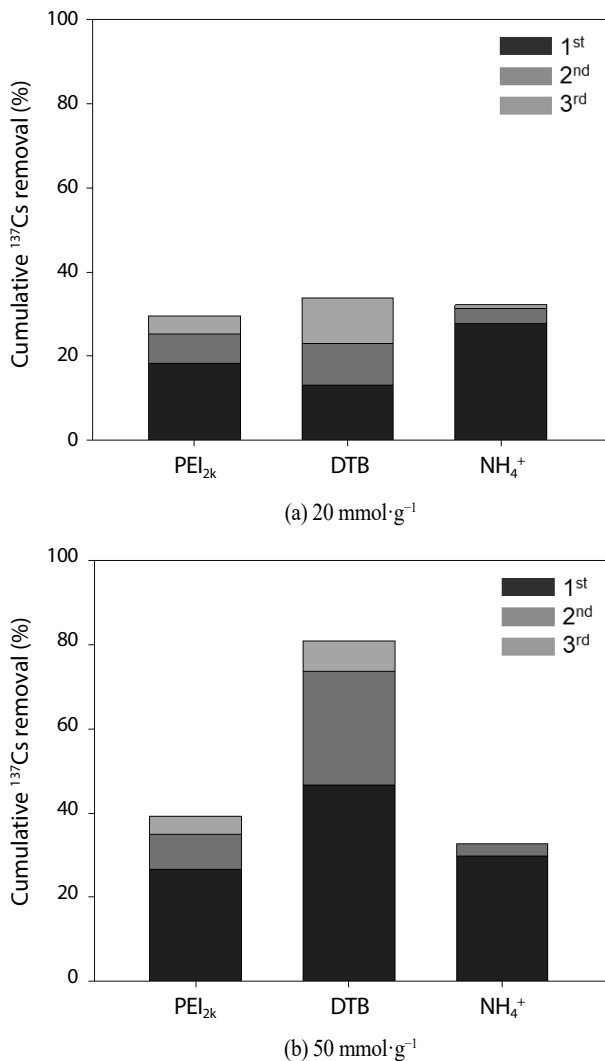
(a) 20 mmol·g⁻¹

(b) 50 mmol·g⁻¹

Fig. 4. Cumulative amounts of radiocesium desorption by repeated treatment of ^{137}Cs-SF250 with desorption agents (20 or 50 mmol·g⁻¹) at 20°C (reaction time of each step: 24 hr).

Cs-selective adsorption sites among the various adsorption sites in soil [6]. For this reason, it is expected that many of the ^{137}Cs ions were bound to the Cs-selective sites, unlike in the previous experimental condition that the amount of the adsorbed Cs exceeded the quantity of expected Cs-selective sites in soil.

Fig. 3 shows the amount of ^{137}Cs desorbed from ^{137}Cs-SF200 by various desorption agents at 20°C. Similar to the previously described experimental result (non-radioactive

Cs desorption), NH_4^+ could desorb a large amount of ^{137}Cs (~27%) from ^{137}Cs-SF200 at pH 3. The PEI_{2k} (~18%), PEI_{25k} (~14%), and HCl (13%) also could desorb significant amounts of ^{137}Cs from the soil. In contrast, the desorption agents containing quaternary ammonium ions were not efficient at desorbing stably bound ^{137}Cs from the soil samples. Furthermore, none of the ^{137}Cs could be desorbed from the soil when ^{137}Cs-SF200 was reacted with deionized water.

Because PEI_{2k}, HCl, and NH_4^+ showed promising results for the desorption of ^{137}Cs from the soil sample, the cumulative amounts of desorbed ^{137}Cs were measured after repeated treatment of the soil samples with desorption agents by replacing the solution every 24 hr (Fig. 4). The amount of desorption agent relative to the amount of soil was 20 mmol·g⁻¹ or 50 mmol·g⁻¹. In the case of the NH_4^+ at pH 3, most exchangeable ^{137}Cs ions were desorbed during the first washing step, and a very small amount of ^{137}Cs was additionally desorbed during the second and third washing steps. Furthermore, the total amount of ^{137}Cs desorbed by two different concentrations of NH_4^+ were almost identical (~32%). In these regards, it is concluded that NH_4^+ is efficient for removing weakly bound Cs in actual soil in a single washing step, but that additional extraction of stably bound ^{137}Cs is inefficient.

In contrast, a significant amount of additional ^{137}Cs could be desorbed from the soil by repetitive treatment with HCl solutions. Moreover, higher concentrations of HCl desorbed much larger amounts of ^{137}Cs from ^{137}Cs-SF200. When ^{137}Cs-SF200 was washed three times with HCl solutions at 20 and 50 mmol·g⁻¹ soil, the total amount of desorbed ^{137}Cs was 35% and 83%, respectively. Unlike the other desorption agents, HCl is known to initiate disintegration of clay minerals [28, 35], and it was reported that Al and Fe elements can be partially dissolved from illite and kaolinite by an HCl solution [36]. It is predicted that the additional desorption of ^{137}Cs by repetitive HCl treatment is related to weakening of the structural integrity of the soil components; thus, more comprehensive study will be required.

In the case of PEI, 40% of ^{137}Cs was desorbed after treatment repeated three times with 50 mmol·g^{-1} soil. Even though the total desorbed ^{137}Cs from the soil sample by PEI was higher than that achieved by repetitive treatment with NH$_4^+$, PEI also showed limited ^{137}Cs desorption because the SF200 sample contained only non-expandable clay minerals of which the interlayers were not accessible using cationic polymers.

4. Conclusions

The behaviors of Cs desorption from clay minerals and actual soil samples were investigated using various Cs-desorption agents, including polymeric cation exchange agents, single molecular cations, and HCl.

First, the desorption of Cs from pure clay minerals, including montmorillonite and illite, and mixed-layer clays of hydrobiotite, vermiculite, and biotite were investigated. The polymeric cation exchange agents (such as PEI and PDDA) could efficiently remove Cs from expandable montmorillonite. The acidic desorption solutions containing HCl or PEI could remove a large amount of Cs from hydrobiotite. However, most desorption agents could desorb only ~54% of Cs from illite because of the specific adsorption of Cs to selective adsorption sites.

The actual soil samples were collected from near a NPP in South Korea and the major minerals in the soil were identified as illite, kaolinite, and quartz. Because a small amount of Cs-selective illite was contained in the soil sample, the total amount of adsorbed ^{133}Cs was larger than the amount at the Cs-selective sites in soil. Thus, desorption of non-selectively bound Cs from the soil seemed to take place mostly during the reaction. Nevertheless, NH$_4^+$ and HCl showed high Cs desorption efficiency in the actual soil samples. In contrast, the ^{137}Cs-adsorbed soil sample had extremely low Cs loading compared to the CEC (2.8×10^{-7}%), and thus most of the adsorbed ^{137}Cs is expected to be located at Cs-selective sites. The total amount of ^{137}Cs desorbed

by repeated washing was related to the desorption agents in the order: HCl > PEI > NH$_4^+$, and HCl efficiently removed ~83% of the radiocesium. It is expected that a synergetic effect between the alteration of minerals by acidic attack and the H$^+$/Cs$^+$ ion exchange reaction promoted desorption of ^{137}Cs. In this regard, mineral alteration agents used in cooperation with a cation exchanger offers a promising washing solution for the remediation of radiocesium-contaminated soils.

Although individual clay minerals exhibited distinguishable behaviors during the desorption of Cs, it was difficult to clearly reveal correlations between the Cs desorption from single clay minerals and that from the example soil samples. Because actual soils display complex behaviors according to their soil compositions and weathering conditions, comprehensive characterizations of actual soil wastes and adsorption/desorption behaviors will be crucial to design successful soil remediation plans.

Acknowledgment

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