Study of Heavily Adhesive Cs in Soil Environment

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Abstract—Two years having passed since the nuclear crisis at Fukushima, radioactive $^{137}$Cs with the half-life of ~ 30 years has come to the forefront of our largest concern. To gain an insight into current unsuccessful $^{137}$Cs decontamination from soil, heavily adhesive Cs adsorption, referred as specific Cs adsorption here, is highlighted for the layered clay minerals. Beside the interlayer Cs$^+$ cations, a population of Cs is able to adsorb on the surfaces of open nanospaces with their sizes of ~ 0.3 nm and ~ 0.9 nm, which are formed by one- and two-clay nanosheet insertion into interlayer spaces. They are adsorbed on the surfaces of both the open nanospaces so strongly that cannot be removed even by the hydrochloric acid solution of pH 1.0, these open nanospaces thus acting as the specific Cs adsorption site. The characteristic local molecular structures as a clay-nanosheet edge and a wedge-shaped frayed part available in the open nanospaces are responsible for the specific Cs adsorption. Radioactive $^{137}$Cs that is not cleaned up after the decontamination work would originate from the specific Cs adsorption clarified here. The present findings unambiguously provide the molecular evidence of specific Cs adsorption and are thus of importance for further sophisticated decontamination of the radioactive Cs from the soil environment.

Index Terms—Clay mineral, positronium, radioactive Cs, soil environment.

I. INTRODUCTION

Following the nuclear crisis at the Fukushima Daichi Nuclear Power Plant triggered by the earthquake off the Pacific coast of Tohoku, Japan, on March 11, 2011 [1], a number of volatile fission products as, e.g., $^{129m}$Te, $^{131}$I, $^{134}$Cs, and $^{137}$Cs have been released into the atmosphere [2]. These radioactive nuclides were carried by wind and fell out on the land surface, by which soil contamination occurs [3]-[5]. Two years having passed, the radionuclide of our largest concern is $^{137}$Cs with the half-life of ~ 30 years because of its harmful influences on human life for decades [6], [7]. The radioactive Cs deposited on the terrestrial areas is estimated to be ~ 22 % of the total release that largely remains in soil [8].

In the soil environment, there exists a wealth of layered clay minerals such as saponite. The layered clay minerals with angstrom-scale interlayer spaces act as the major sorbents of radioactive Cs from the following reasons [9]. The layers of clay minerals are negatively charged originating from local compositional deviation, which is generally balanced with alkali cations, such as Na$^+$, Li$^+$, and Cs$^+$ in the interlayer spaces (see Fig. 1). The Cs$^+$ cation has a radius of ~ 1.8 Å larger than those of other alkali cations, being less hydrated with water molecules to go outside the interlayer spaces. Furthermore, there exists a hexagonal cavity with the size of ~ 2.6 Å on the layer surface, which is suitable for capturing the Cs$^+$ cation. It is thus normally accepted that the layer surface of clay minerals is adsorption sites for radioactive Cs.

Off-site decontamination of radioactive nuclides has been extensively attempted by municipalities, such as Fukushima city, under the instruction of the Ministry of the Environment (MOE), but there seems to be little progress in the radioactive Cs [10]. According to the results of radiation monitoring survey by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), many hot spots as for the radioactive Cs exceeding the provisional reference value still remain inside and outside Fukushima [11]. It has been reported that the decontamination works performed as the model project of clean-up methodology drawn up by MOE and Japan Atomic Energy Agency (JAEA) significantly reduces the dose rate but does not achieve the safety level down to the annual dose of ~ 20 mSv [12]. Indeed, the decontamination works did not allow the reduction of the radioactive Cs below the reference value in the surveyed field of ~ 6.5 % in Iwate prefecture [13]. These facts imply the presence of Cs adsorption strong enough not to be cleaned by conventional decontamination, which is referred as specific Cs adsorption hereafter.

Our recent studies for the layered clay minerals by positronium (Ps) lifetime spectroscopy coupled with molecular dynamics (MD) simulation revealed the local molecular structures, in which one- and two-clay nanosheets are inserted into the interlayer spaces forming open nanospaces [14]. These molecular sites have not been identified by other microscopic techniques, as e.g., transmission electron microscopy and x-ray diffraction, thus having been unconsidered for the molecular model of inorganic layered materials so far. Aside from that, we have developed analytical technique employing element-specific Ps that probes elements located on the surface of open nanospaces [15-18]. This technique is particularly sensitive to Cs as already demonstrated for the analysis of Cs cluster

Fig. 1. Schematic illustration of Cs$^+$ adsorption on the layer surface of clay mineral.
on the surfaces of open nanospaces in SiO₂ glass [15]. In this study, Cs adsorption on the local molecular sites as stated above is highlighted based on the results of element-specific Ps annihilation spectroscopy. The specific Cs adsorption site is explored to answer the current concern: Why is the radioactive Cs not cleaned up after the decontamination work?

II. EXPERIMENTS

Synthetic Na-type saponite Na₁₀₀₆₅[Me₅₋₅₂Li₂₋₅₆]Si₇₆O₂₀[OH]₄ produced by Kunimine Industries Co. Ltd., Japan, was employed as Cs-unloaded sample. The particle size is approximately 20 nm. Cs loading was conducted by impregnating the Na-type saponite with 1 M aqueous solution of CsCl. All the samples were initially treated at 423 K for 24 h under the vacuum condition of ~ 10⁻⁵ Torr, which are referred as starting samples.

The sizes of open nanospaces and their fractions were investigated by Ps annihilation lifetime spectroscopy. A fraction of energetic positrons injected into samples forms the bound state with an electron, Ps. Singlet para-Ps (p-Ps) with the spins of the positron and electron antiparallel and triplet ortho-Ps (o-Ps) with parallel spins are formed at a ratio of 1 : 3. Hence, three states of positrons: p-Ps, o-Ps, and free positrons exist in samples. The annihilation of p-Ps results in the emission of two γ-rays of 511 keV with lifetime ~ 125 ps. Free positrons are trapped by negatively charged parts, such as polar elements, and annihilated into two photons with lifetime ~ 450 ps. The positron in o-Ps undergoes two-photon annihilation with one of the electrons bound to surrounding molecules with a lifetime of a few ns after localization in angstrom-scale pores. The last process is known as o-Ps pick-off annihilation and provides information on the open nanospace size R through its lifetime τ_{o-Ps} based on the Tao-Eldrup model [19-20]:

\[ \tau_{o-Ps} = 0.5 \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1} \tag{1} \]

where \( R_0 = R + \Delta R \), and \( \Delta R = 0.166 \text{ nm} \) is the thickness of homogeneous electron layer in which the positron in o-Ps annihilates. The positron source (⁵²Na), sealed in a thin foil of Kapton, was mounted in a sample-source-sample sandwich. The starting samples (dehydrated samples) were exposed to hydration. It is thus unlikely that the open space A with the constant size of ~ 0.3 nm corresponds to the interlayer spaces. The open space B with its size ranging from ~ 0.6 to ~ 1 nm is in turn too large to relate with the interlayer spaces. We thus introduced two kinds of local molecular structures simulated in turn too large to relate with the interlayer spaces. We thus introduced two kinds of local molecular structures simulated by molecular dynamics (MD) calculations to explain the long-term variation of open nanospaces observed for the Cs-unloaded saponite in Fig. 2 [14]. One of the molecular structures is called type A, in which a one-clay nanosheet is inserted into the interlayer spaces forming the open space with the size of ~ 0.3 nm (see inset in Fig. 2 (a)). Another is

III. RESULTS AND DISCUSSION

Ps lifetime spectroscopy for both the Cs-unloaded and loaded samples yields four components of lifetime, where the longest and the second longest components with their relative intensities were attributed to pick-off annihilation of o-Ps localized in the open nanospaces denoted as A and B. In Fig. 2, the sizes \( R_A \) and \( R_B \) evaluated through above the lifetimes based on Eq. (1) are presented together with their relative intensities, in this work called fractions \( f_A \) and \( f_B \), as a function of exposure time. It is well seen that the variations of open spaces with exposure time make responses upon Cs loading. The open space size \( R_A \) is consistently ~ 0.3 nm without any significant change with exposure time for both the Cs-unloaded and loaded samples. The Cs-unloaded sample exhibits decrease in the open space size \( R_0 \) from ~ 0.9 nm to ~ 0.6 nm along with exposure time, whereas the size \( R_B \) for the Cs-loaded sample decreases down to ~ 0.7 nm more slowly. The fraction \( f_A \) for the Cs-unloaded sample increases from ~ 5 % to ~ 15 % with exposure time in contrast to the decrease of the fraction \( f_B \) from ~ 10 % to ~ 2 %, which are synchronized with the variation of \( R_B \) in the time scale of ~ 10 days. The Cs-loaded sample exhibits the increase in the fraction \( f_A \) in a similar manner to that of Cs-unloaded one but in much longer time scale of ~ 19 days. The fraction \( f_B \) initially exhibiting high value of ~ 20 % decreases down to ~ 3 % synchronizing with the increase of \( f_A \).

Generally, the interlayer spaces expand together with hydration. It is thus unlikely that the open space A with the constant size of ~ 0.3 nm corresponds to the interlayer spaces. The open space B with its size ranging from ~ 0.6 to ~ 1 nm is in turn too large to relate with the interlayer spaces. We thus introduced two kinds of local molecular structures simulated by molecular dynamics (MD) calculations to explain the long-term variation of open nanospaces observed for the Cs-unloaded saponite.
type B, in which a two-clay nanosheet is inserted into the interlayer spaces forming the large open space with the size of ~ 0.9 nm (see inset in Fig. 2 (c)). Note that the sizes of open spaces simulated by MD calculations are in agreement with those observed by Ps annihilation spectroscopy. In a dehydrated state, the local molecular structure of type B dominantly exists as deduced from the higher fraction of $f_B$. H$_2$O molecules adsorbed at Na$^+$ cations in the interlayer spaces due to hydration trigger off the onset of rheological motion of nanosheets in parallel to the layer direction. One of two nanosheets inserted into the interlayer space of type B is thus released away, with the type A with smaller open spaces getting to dominant for a hydrated state. The open space size $R_B$ thus decreases with increasing exposure time, though the open space size $R_A$ remains constant. Correspondingly, the fraction $f_B$ decreases and the fraction $f_A$ oppositely increases with exposure time.

![Fig. 2. Sizes of open spaces (a) $R_A$ (solid circles) and (c) $R_B$ (solid triangles) with their fractions (b) $f_A$ (open circles) and (d) $f_B$ (open triangles) as a function of exposure time obtained for the Cs-loaded saponite sample. The data for the Cs-unloaded sample taken from our literature (14) is added for comparison. Types A and B are schematically illustrated in (a) hydrated and (b) dehydrated saponite. The solid lines are drawn for guiding the eye. Note that the types A and B dominantly exist in (a) hydrated and (b) dehydrated saponite. The open spaces A and B thus acting as specific Cs adsorption site for Cs. To confirm it, the elemental analysis of open spaces A and B by AMOC spectroscopy was again conducted for the Cs-loaded sample, which was washed by the hydrochloric acid solution of pH 1.0 strong enough to decontaminate the radioactive Cs [25]. Noticeable here is that the pore surface parameters are unchanged before and after washing by hydrochloric acid solution for both the cases of open spaces A and B (see Fig. 3). This evidences that Cs adsorbed on the surfaces of both open spaces A and B cannot be removed even by the strong acid, the open spaces A and B thus acting as specific Cs adsorption sites.](image)

![Fig. 3. Positron-age dependent pore surface parameters for (a) hydrated and (b) dehydrated samples measured by AMOC spectroscopy. The data for Cs-unloaded, Cs-loaded, and then acid-washed saponite are indicated with open circles, solid triangles, and open triangles in both (a) hydrated and (b) dehydrated saponite. The solid lines are drawn for guiding the eye. Note that the types A and B dominantly exist in (a) hydrated and (b) dehydrated saponite. The data shown in (a) and (b) are thus exclusively resultant from the elemental environment of open spaces A and B, respectively.](image)

It is now recognized that Cs adsorbs on the surfaces of the open nanospaces A and B in the local molecular structures of types A and B revealed by a series of Ps annihilation spectroscopy. Our next interest is whether the open spaces A and B act as specific adsorption site for Cs. To confirm it, the elemental analysis of open spaces A and B by AMOC spectroscopy was again conducted for the Cs-loaded sample, which was washed by the hydrochloric acid solution of pH 1.0 strong enough to decontaminate the radioactive Cs [25]. Noticeable here is that the pore surface parameters are unchanged before and after washing by hydrochloric acid solution for both the cases of open spaces A and B (see Fig. 3). This evidences that Cs adsorbed on the surfaces of both open spaces A and B cannot be removed even by the strong acid, the open spaces A and B thus acting as specific Cs adsorption sites.
adsorption sites. It should be noted here that there exist the clay-nanosheet edge sites in both the open spaces A and B. The clay-nanosheet edge sites are expected to be chemically active for molecular adsorption as those of cup-stacked carbon nanotube. Furthermore, the wedge-shaped part similar to the frayed-edge site generally appeared after long-term pedogenetic weathering is already available both in the open spaces A and B. The frayed-edge site is known to capture Cs with much greater affinity than the expanded layers [7,26]. It is reasonably inferred that such local molecular sites characteristic for the open spaces A and B are responsible for the heavily adhesive Cs adsorption observed here.

Based on the present findings by element-specific Ps annihilation spectroscopy for the Cs-unloaded and Cs-loaded saponite samples, the following adsorption behavior is presumed for the radioactive Cs in soil. As is generally accepted, the radioactive Cs selectively adsorbs on the surface of interlayer spaces in clay minerals. Such physisorbed Cs on the clay surface could be removed by the conventional decontamination work as, e.g., high-pressure water jet cleaning. In addition, a population of Cs adsorbs on the surfaces of both open spaces A and B formed by inserting one- and two-clay nanosheets into the interlayer spaces, respectively. The one- and two-nanosheet inserted local molecular structures of types A and B dominantly exist in hydrated and dehydrated states, respectively, thus implying that both the molecular structures favorably appear under a wide variety of hydration conditions in soil. Cs adsorbed on the surfaces of both the open spaces A and B is so adhesive that cannot be removed even by the hydrochloric acid solution of pH 1.0. There exists characteristic local molecular site as a wedge-shaped part both in the open spaces A and B, where the hexagonal cavities similar to the size of Cs+ cations are faced each other. It is expected that this molecular site strongly captures Cs+ cations, being responsible for the specific Cs adsorption. In addition to that, the open space B possesses the chemically-active molecular site as a clay-nanosheet edge. The open spaces A and B thus act as the specific Cs adsorption site, where conventional decontamination could not be applied. Radioactive 137Cs that still appears beyond the reference value after the decontamination work would originate from the specific Cs adsorption clarified in the present work.

IV. CONCLUSION
To gain an insight into current unsuccessful decontamination of radioactive 137Cs from soil, the adsorption sites of heavily adhesive Cs were investigated for the layered clay mineral by means of element-specific Ps annihilation spectroscopy. Beside the interlayer Cs+ cations, a population of Cs is able to adsorb on the surfaces of open nanospaces A and B with their sizes of ~ 0.3 nm and ~ 0.9 nm, which are formed by inserting one- and two-clay nanosheets into the interlayer spaces. The open space B is found to be more susceptible to Cs adsorption than in the open space A owing to its larger size. Cs adsorbs on the surfaces of both the open nanospaces A and B thus acting as the specific Cs adsorption site. The characteristic local molecular sites as a clay-nanosheet edge and a wedge-shaped frayed part available in the open spaces A and B could be responsible for the specific Cs adsorption. Such heavily adhesive Cs could not be removed by the conventional decontamination work. The local molecular structures of types A and B dominantly exist in hydrated and dehydrated states, respectively, thus implying that both the molecular structures favorably appear under a wide variety of hydration condition in soil. The present findings unambiguously provide the molecular evidence of specific Cs adsorption and are thus of importance for further sophisticated decontamination of the radioactive Cs from the soil environment.

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REFERENCES
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