



# Enhanced desorption of cesium from collapsed interlayer regions in vermiculite by hydrothermal treatment with divalent cations



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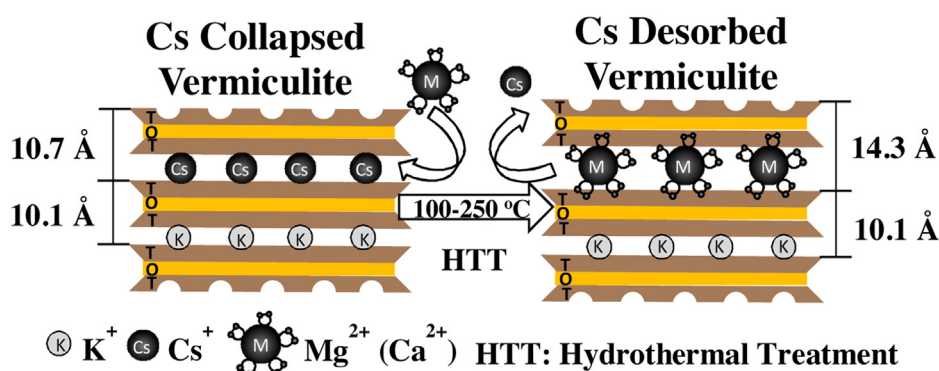
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## HIGHLIGHTS

- Desorption of Cs<sup>+</sup> fixed in collapsed interlayer region of vermiculite was studied.
- Monovalent cations readily induced interlayer collapse inhibiting Cs<sup>+</sup> desorption.
- Larger hydrous ionic radii of divalent cations greatly prevented Cs<sup>+</sup> desorption.
- Effect of divalent cation on Cs<sup>+</sup> desorption changes depending on thermal treatment.
- ~100% removal of saturated Cs<sup>+</sup> was achieved by hydrothermal treatment at 250 °C.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Adsorption of cesium (Cs) on phyllosilicates has been intensively investigated because natural soils have strong ability of immobilizing Cs within clay minerals resulting in difficulty of decontamination. The objectives of present study are to clarify how Cs fixation on vermiculite is influenced by structure change caused by Cs sorption at different loading levels and how Cs desorption is affected by various replacing cations induced at different treating temperature. As a result, more than 80% of Cs was readily desorbed from vermiculite with loading amount of 2% saturated Cs ( $5.49 \times 10^{-3} \text{ mmol g}^{-1}$ ) after four cycles of treatment of 0.01 M  $\text{Mg}^{2+}/\text{Ca}^{2+}$  at room temperature, but less than 20% of Cs was desorbed from saturated vermiculite. These distinct desorption patterns were attributed to inhibition of Cs desorption by interlayer collapse of vermiculite, especially at high Cs loadings. In contrast, elevated temperature significantly facilitated divalent cations to efficiently desorb Cs from collapsed regions. After five cycles of treatment at 250 °C with 0.01 M  $\text{Mg}^{2+}$ , ~100% removal of saturated Cs was achieved. X-ray diffraction analysis results suggested that Cs desorption was completed through enhanced diffusion of  $\text{Mg}^{2+}$  cations into collapsed interlayer space under hydrothermal condition resulting in subsequent interlayer decollapse and readily release of Cs<sup>+</sup>.

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## 1. Introduction

Following the accident at Fukushima Dai-ichi Nuclear Power Plant (FDNPP) in March 11, 2011, radioactive Cs ( $^{137}\text{Cs}$  and  $^{134}\text{Cs}$ ) have widely contaminated the area around the northern Kanto and

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Tohoku regions in Japan [1,2]. Since Cs isotopes are mainly retained within the surface 5 cm of the soil as a result of their selective sorption on clay minerals, topsoil had been extensively stripped and therefore large amount of contaminated soils (18.7–28 million m<sup>3</sup>) has been generated and accumulated from the primary decontamination activities, most of which currently are stored at several temporary storage sites and being transferred to interim storage facility (ISF) for further treatment prior to final disposal [3,4]. Subsequently, the remediation of these cumulated hazardous soils and their volume reduction have become the subject of renewed attention.

To date, the uptake properties of Cs in soils have been sufficiently clarified [5–7]. According to various models, spectroscopic detection and conceptual simulation, it is well documented that Cs generally interacts strongly and selectively with the 2:1 phyllosilicate fractions of soils [8–13]. In Fukushima, it is suggested that clay mineral composition of the soils consists to some extent of vermiculite (or vermiculitized biotite), which has a dominant Cs sorption selectivity and high sorption capacity, in comparison with other clay minerals (fresh biotite, illite, smectite, kaolinite, halloysite, allophane, imogolite) [14–16]. Thus, vermiculite represented one of the most concerned clays in relation to Cs retention in Fukushima soils. Regarding to Cs fixation on vermiculite, recent studies proved that Cs<sup>+</sup> would be incorporated into the interlayers of vermiculite by exchange with preexisted hydrated cations and fixed at the centers of six-membered rings in the upper and lower SiO<sub>4</sub> tetrahedral sheets across the interlayer [17–20]. Moreover, these sorbed Cs<sup>+</sup> ions tend to concentrate to some hydrated interlayer space rather than distribute homogeneously in all hydrated interlayers by forming mixed-ionic interlayers with hydrated Mg<sup>2+</sup>/K<sup>+</sup> [17,21]. As a result, progressively accumulated Cs<sup>+</sup> ions in monoionic Cs<sup>+</sup> interlayers will further produce the interlayer dehydration, which readily induces a layer collapse making Cs tightly fixed by shielding of two closer adjacent layers for its high immobilization [8,9,21,22].

Considering the actual conditions of Cs contamination in Fukushima soils (about 10<sup>-12</sup>–10<sup>-10</sup> mol/kg), Cs will be mainly sorbed by partially weathered micaceous minerals on frayed edge sites (FES) [17–26]. Even in trace amounts, the Cs trapped by FES of partially-vermiculitized biotite/phlogopite or illite/muscovite clays, will readily change the local force and increase attraction of two planar-edge ends with stable structure, leading to form an inner-sphere Cs complex fixed in edge-collapsed interlayer positions [8,9]. Moreover, it is also suggested that such fixed Cs may not only be retained at the edges, but possibly diffuse into deeper interior space by topotactic-exchange with adjacent cations over longer term [12,20]. If that was the case, considering complexity of clay composition in soils and heterogeneous distribution of Cs on various clays, sorbed Cs in actual contaminated soils would possibly not only associate on clay planar/edge sites but also intercalate within collapsed FES/interlayer sites, which might be therefore comparable with the Cs fixation in collapsed interlayer region of vermiculite induced by Cs sorption at high loading amount.

In view of the Cs<sup>+</sup> binding on clays/soils being due largely to exchange-sorption, desorption of Cs based on cation-exchange would be a plausible way, as done in numerous previous studies [27–36]. On one hand, some of these studies indicated that most of sorbed Cs on vermiculite/smectite at low loading level without forming dominant interlayer collapse could be readily desorbed [31–34]. However, once Cs<sup>+</sup> was sorbed by partially-vermiculitized biotite or illite/micaceous followed with readily edge-interlayer collapse, it could be only poorly and partially desorbed even by drastic desorption treatments of the clays/soils under high concentration of various electrolytes [14,27–30]. On the other hand, regular desorption of Cs would be a kinetic process over long term, which may potentially take days to even years to reach an equilibrium state for desorption [37,38]. The slow diffusion of Cs through

topotactic exchange with adjacent ions, especially aggravated by interlayer collapse near the dehydrated Cs<sup>+</sup>, is generally believed to be the main cause of the kinetic results [37,38]. As a standard Cs decontamination technology has not been unequivocally established currently, it is critically necessary that investigations with more efficient Cs<sup>+</sup> desorption could be attempted in order to satisfactorily remediate the Cs-contaminated soils in Fukushima [39–41].

In our previous work, we elucidated that Cs intercalated in vermiculite was effectively desorbed by exchange with various cations in seawater [42]. The most notable finding is that hydrothermal treatment of the Cs sorbed vermiculite with seawater could greatly promote desorption efficiency while details of desorption process by each cation are not completely clear. In present study, we further attempt to report this novel technical method to efficiently desorb Cs<sup>+</sup>, especially from the collapsed interlayer regions of vermiculite. Herein, the refinement of desorption process with mechanism classification is of critical importance.

## 2. Experimental

### 2.1. Materials

The used vermiculite (termed as Verm) sample, a 2:1 phyllosilicate clay mineral, was purchased from Vermitech Co. Ltd, Japan. The dry sample was firstly characterized by scanning electron microscope (Fig. S1 in Supplementary material) and analyzed by X-ray fluorescence (XRF) (Table S1 in Supplementary material). It is a kind of Mg-type vermiculitized biotite originated from South Africa and has an interstratification structure consisting of Verm layers and mica layers [42]. Same with other South African kinds of vermiculites, its regular physical, chemical and mineralogical properties had been similarly reported elsewhere [17,31,32]. Verm particles were firstly sieved to size of 250–710 μm and washed using distilled water for 5 times to dissolve the impurities. Then, the samples were dried in an oven at 40 °C prior to the experiment. Reagent grade CsCl was purchased from Wako Pure Chemical Industries, Japan and employed without further purification. All other used reagents were of analytical grade (or higher).

### 2.2. Adsorption experiments

The Cs adsorption on Verm was measured in polyethylene test tubes at ambient temperature with batch method. We prepared two Cs-sorbed Verm specimens at low and high loading levels (denoted as Verm-low and Verm-high, respectively). In detail, Verm (1 g) was equilibrated in 0.1 L of solutions containing 0.1 mM NaCl, 0.075 mM CsCl for low loading level, and 7.5 mM CsCl for high loading level during 38 days with continuous stirring. After achieving sorption time, suspension was centrifuged and the supernatant was separated from the solid particles by filtering through membrane filter of 0.2 μm. Cs sorbed Verms were dried at 75 °C for 24 h while the Cs<sup>+</sup> amount remaining in filtrate was measured by atomic absorption spectroscopy (AAS, SpectrAA-6200, Shimadzu Corp). The adsorption quantity of Cs<sup>+</sup> thus obtained were calculated as 5.49 × 10<sup>-3</sup> mmol g<sup>-1</sup> and 2.69 mmol g<sup>-1</sup> to Verm-low and Verm-high samples, corresponding to 2% and 100% of the saturation amount, respectively.

### 2.3. Desorption experiments

We carried out the desorption experiments in two different procedures (i.e. ambient and hydrothermal desorption treatments). During two procedures, desorption treatment was conducted according to a sequential extraction method, which allows to indicate the inefficiency of a single treatment and to identify some

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