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研究課題名(和文) 微生物起源Mn酸化物による放射性Csの新規固定機構の解明

研究課題名(英文) Exploring a new fixation mechanism of radioactive Cs by biogenic Mn oxide

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研究成果の概要(和文)：Mn酸化物への放射性Csの吸着と脱離行為に系統的分析を行った。Mn酸化物の表面に、マルチサイトの吸着を存在しているのを発見した。微生物起源Mn酸化物の表面微量平衡電荷イオンの存在は、低濃度放射セシウムへの吸着には強烈な影響がある。層状Mn酸化物と比較すると、トンネル状Mn酸化物は特異的な吸着挙動を示した。このような吸着挙動の違いは、層状とトンネル状Mn酸化物の構造の違いが影響していると考えられる。

研究成果の概要(英文)：Mn oxide is known to be a scavenger for metallic ions in nature. By using radioactive Cs as an isotope tracer, this work investigated the sorption and desorption behavior of Cs on Mn oxides with different structures over a wide range of concentrations. Multiple sorption sites were observed on both layer and tunnel type Mn oxides. Trace amount of competitive ions located at the surface of biogenic birnessite affected Cs sorption at low concentrations. Sorption sites with high Cs affinity were observed on tunnel type Mn oxide, which implied their possible role on the fixation of Cs in environment.

研究分野：原子力学

キーワード：Cs decontamination biomaterial Mn oxide XAFS

1. 研究開始当初の背景

The accident at Fukushima Daiichi nuclear power plant resulted in an abrupt release of huge amounts of Cs into the environment. From previous report, Cs migration is mostly controlled by sorption onto clay mineral through ion exchange. For clay, Cs uptake is largely affected by the presence of mica-like minerals, since these minerals offer sorption sites with high selectivity for Cs, which are called “frayed edge sites”.

Mn oxide is known to be a scavenger for metallic ions in nature, because it has a large specific surface area, and low point of zero charge. Mn oxides are ubiquitous in soil, which may also influence the migration of radioactive Cs in Fukushima forest.

Mn oxides in natural environment have a variety of structures. Todorokite and birnessite are two of the more common Mn oxide minerals in terrestrial deposits which could be determined by X-ray diffraction and rietveld refinement. Todorokite has a tunnel structure composed of triple chains of MnO₆ octahedra. The triple chains share corners to form 3×3 tunnels. Lower valence cations (e.g. Mn(III), Ni(II), and Mg(II)) are located at the edge sites of the triple chains, substituting for Mn(IV) to counterbalance charges on the tunnel cations. Birnessite has a layer structure with a unit sheet of MnO₆ octahedra. The interlayer cation such as K⁺, Na⁺, or Mg²⁺ and water molecules occupied the interlayer sites with different locations. Birnessite could participate in a variety of redox and cation exchange reactions in soil and groundwater. Thus, the presence of birnessite may affect the geochemical cycling of elements in the environment.

In the past five years, sorption mechanism of Cs by Mn oxides with different structures has been studied by using chemical and spectroscopic methods. According to the results from synchrotron-based XRD and XAFS analysis, Cs ions were reversibly sorbed on Mn oxides. And most of the sorbed Cs formed outer-sphere complex. However, all these experiments used a high concentration of Cs, which could not describe the sorption behavior of radioactive Cs at ultralow concentrations. It is necessary to investigate the sorption behavior of radioactive Cs with a wide range of concentrations.

2. 研究の目的

The purpose of the present work is to clarify the new fixation mechanisms of radioactive Cs by Mn oxide with different structures. Although Cs sorption onto birnessite and todorokite has been studied before, all of these studies described sorption with high Cs concentration, with the variation of one or several parameters. No sorption model capable of comprehensively interpreting Cs uptake.

In the work, three controversial points for the interpretation of some features of Cs sorption onto birnessite as well as todorokite are discussed: (1) the non-linear feature of the sorption isotherm base on a very large set of experimental sorption data under a wide range of Cs concentrations (10⁻¹⁰ to 0.1M); (2) the variation of selectivity coefficients as a function of the ionic strength; and (3) the relationship between the structural feature of Mn oxide and their sorption behaviors.

3. 研究の方法

(1) preparation of Mn oxides

To prepare biogenic birnessite, Mn(II)-oxidizing fungus *A. strictum* KR21-2 were incubated in medium containing (per L) 1mmol MnSO₄, 3 mmol sodium acetate, 150 mg yeast extract, 200 μmol MgSO₄·7H₂O, 50 μmol CaCl₂·2H₂O, 80 μmol H₃BO₃, 7.4 μmol FeCl₃·6H₂O, 3.0 μmol ZnSO₄·7H₂O, 2.4 μmol Na₂MoO₄·2H₂O, 0.04 μmol CuSO₄·5H₂O, and 20 mmol HEPES buffer solution (pH 7.0). In some of the experiments, 0.4 mmol/L ZnSO₄ or NiSO₄ were added during incubation. After one week incubation, the product were collected by centrifuge, washed with pure water, resuspended in HCl solution (pH = 2) for 12 hours, and freeze dry. δ-MnO₂ were prepared according to Villalobos et al. (2003). Todorokite were prepared according to Feng et al. (2004).

The structure of all prepared materials were characterized by XRD and Mn K-edge XAFS spectroscopy.

(2) Radionuclide

The radionuclide ¹³⁷Cs was used in this experiment as a radioisotope tracer. Cs activity in solution was measured by liquid scintillation counting.

(3) Sorption experiments

Sorption isotherms were collected with Cs concentration varying from 1×10⁻¹⁰ M to 0.1 M. ¹³⁷Cs was added in all samples as a radio isotope tracer. All samples were sealed and maintained with continuous shaking for 2 days. They were then centrifuged, and the activity of Cs in the supernatant solution was measured. No significant Cs adsorption in the tubes was measured. The distribution coefficient, K_d, was calculated with the following:

$$K_d = \frac{C_0 - C_t}{C_t} \times \frac{1}{m_{\text{sorbent}}}$$

C₀ is the total Cs concentration of the suspension (mol/L); C_t is the Cs concentration in solution at equilibrium (mol/L); and m_{sorbent} is the Mn oxide concentration (g/mL).

(4) Modeling background.

All calculations were performed with PHREEQC. The ionic exchange reaction is expressed as follows:

$Z_B A \equiv X + Z_A B \Leftrightarrow Z_A B \equiv X + Z_B A$
 the cation exchange reaction can be described with selectivity coefficients. According to the Gaines and Thomas definition, the selectivity coefficient is expressed by

$${}^B A K_{sel} = \frac{(N_B)^{Z_A} (\alpha_A)^{Z_B}}{(N_A)^{Z_B} (\alpha_B)^{Z_A}}$$

The terms α_A and α_B are the activities of the cation A and B, and N_A and N_B are the equivalent fractional occupancies. The equivalent fractional occupancy is defined as the sorbed quantities of the cations per mass divided by cation exchange capacity.

4. 研究成果

(1) Characterization of Mn oxides

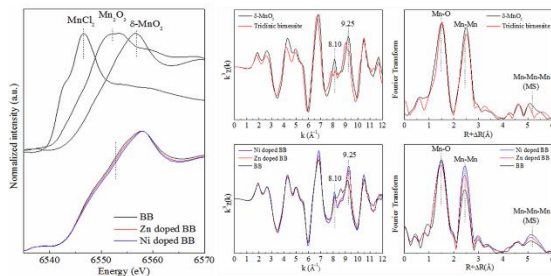


Fig. 1 Mn K-edge XAFS analysis of prepared biogenic Mn oxide.

Using microorganisms, biogenic birnessites (BB) with different structures in molecular scale was prepared. According to Mn K-edge XANES analysis, the Mn average oxidation state increased in the order of BB < Zn doped BB < Ni doped BB. According to Mn K-edge EXAFS analysis, doping of Zn or Ni increased the number of layer vacant site. And the number of layer vacant site increased in the order of: Ni doped BB > Zn doped BB > BB.

As showed in Fig. 2, the EXAFS spectra of todorokite and birnessite show similar amplitude. A clear peak splitting was observed at 7.9 \AA^{-1} and 9.1 \AA^{-1} , which is common to todorokite structure.

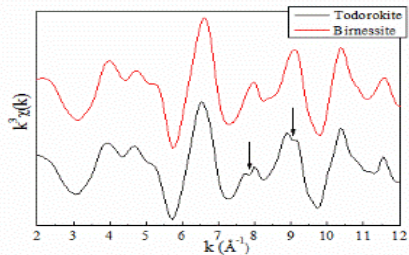


Fig. 2 Mn K-edge EXAFS spectra of birnessite, and todorokite.

(2) Sorption isotherms

Fig. 3 shows the sorption isotherm obtained with Ni doped BB, Zn doped BB, and BB carried out with suspensions at an ionic strength of $I = 1 \text{ mol/L}$ and 1 mmol/L , respectively. In all the birnessite samples, Cs sorption slightly deviated

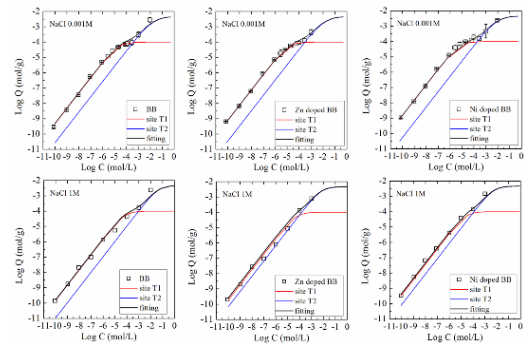


Fig. 3 Cesium adsorption isotherms for the three biogenic birnessites at different ionic strength.

from linearity, implying the existence of two different sorption sites. The saturation of type 1 sites is evidenced by the small plateau observed in sorption data presented in Fig. 3. Up to the saturation of these sites, sorption is linear. After saturation of type 1 sites, another region of linear sorption can be clearly observed. This is in agreement with the presence of type 2 sorption sites. Type 2 sites have lower affinity but higher capacity than type 1 sites. The structural properties influence Cs sorption behavior. The selectivity coefficients increased with the number of layer vacant sites.

The sorption isotherm for Todorokite was clearly deviated from linearity, indicating the existence of two sorption sites with different affinities. The selectivity coefficients of type 1 sites is clearly higher than type 2 sites. This result is consistent with the data obtained from sequential extraction.

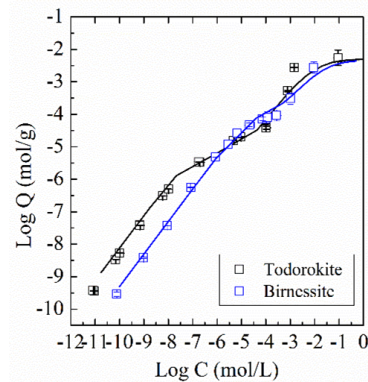


Fig. 4 Cesium adsorption isotherms for synthetic birnessite and todorokite.

(3) Effect of ionic strength on sorption isotherm

Sorption of Cs as a function of the ionic strength was tested. At all ionic strength, sorption isotherms show two regions with different distribution coefficients. For todorokite, Cs sorption increases as the ionic strength of the electrolyte decrease. The experimental result is well consistent with the theoretical data. For biogenic birnessite, K_d values are generally lower than the predicted one. This deviation from the

theoretical behavior is more pronounced at lower ionic strengths. We hypothesize that this phenomenon is caused by competition for sorption sites of the existing trace ions in solution. Base on ICP-OES analysis, trace elements, including K^+ and Mn^{2+} , are present in solutions equilibrated with the biogenic birnessite. The influence of those trace elements could not be ruled out at ultralow Cs concentrations.

5. 主な発表論文等

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6. 研究組織

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