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# Sorption site capacities for Cs on the sedimentary rock in Horonobe area

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## ABSTRACT

The sorption behavior of radionuclides depends on the content of minerals in geological media. The sorption of radionuclides on minerals has been interpreted as the uptake on the sorption sites on mineral surfaces. However, conventional investigations such as X-ray diffraction analysis cannot avoid large errors in quantification of minerals. Furthermore, the discrepancies of sorption behavior have been often found even on the same kind of minerals. Therefore, the sorption site capacity cannot be effectively estimated by the quantification of minerals. In this study, the sorption site on sedimentary rock sampled in Horonobe area, where the Horonobe Underground Research Center, JAEA, is located, was estimated from the Cs sorption isotherms obtained by sorption experiments. To deduce the fitting parameters, illite content estimated from the amount of extracted K by alkylammonium treatment and smectite content estimated from the cation exchange capacity measurement were introduced to the fitting procedure. The result shows that the sorption site capacities of smectite and illite in the sedimentary rock in Horonobe area are 1.3–1.7 $\times 10^{-4}$ and 1.4–4.0 $\times 10^{-5}$ eq/g, respectively.

## 1. Introduction

In geological disposal of radioactive waste, the radionuclides contained in the waste dissolve into groundwater and then migrate to the human environment through geological media. During the migration, the radionuclides will be retarded by the sorption on minerals and the diffusion into rock matrix. As the sorption behavior is one of the key processes to determine the retardation of radionuclides, the reliable estimation of sorption behavior has been required for the safety assessment of geological disposal (e.g., JNC, 2000).

The sorption behaviors of radionuclides have been widely investigated for various kinds of minerals. The sorption of radionuclides on minerals has been interpreted as the uptake on the sorption sites on mineral surfaces such as the formation of surface complexes and cation exchange by the fixed negative charge on the mineral surface. Based on this interpretation, thermodynamic sorption models have been developed to predict the sorption behavior of radionuclides (e.g. OECD/NEA, 2001). The thermodynamic models can estimate quantitatively the effects of aqueous condition on the sorption behavior of radionuclides. Meanwhile, the sorption site capacity on the mineral surface, which serves as an important model parameter, should be quantified with high accuracy for the reliable prediction.

In the actual environment of disposal, the geological media possibly contain more than one kind of minerals. In such geological media, the minerals which contribute to the sorption of radionuclides should be identified among all minerals contained. Moreover, the sorption sites on the surface of these minerals should be quantified. However, conventional investigations such as X-ray diffraction (XRD) analysis cannot avoid large errors in quantification of minerals because of the differences in chemical composition and crystallinity between the minerals contained in the measurement samples and the standard specimen. In addition, the discrepancies of sorption behavior have been often found even for the same kind of minerals. Thus, the sorption site capacity cannot be efficiently estimated based on the quantification of minerals. Therefore, the method to quantify the sorption site capacity should be investigated for the application of sorption models on the safety assessment. In particular, the geological media where several minerals contribute to the sorption of radionuclides should be fully discussed.

In this study, the sedimentary rock in Horonobe area, where Horonobe Underground Research Center, JAEA, is located, was selected as a complex geological medium containing several kinds of minerals. The sorption behavior on the sedimentary rock in Horonobe area has been investigated and found to be dependent on the contents of illite and smectite contained in the rock (Tachi et al., 2009). Tachi et al. (2009) explained the sorption behavior by a sorption model considering the contribution of illite and smectite. However, the sorption site capacities of these minerals were not investigated in detail. Therefore, in this study, sorption experiments were carried out as a function of Cs concentration to investigate the capacity of sorption sites on the minerals. KCl and NaCl were used as background electrolytes to investigate the

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difference of Cs sorption isotherm depending on the type of competitive cation. As the sorption behavior of Cs has been widely studied, the sorption sites of Cs on the minerals and their selectivity coefficients have been established to a considerable extent. Therefore, the sorption site capacities in the sedimentary rock are considered to be quantified from the Cs sorption isotherms. In addition to the sorption experiments, illite content in the sedimentary rock was estimated from the K content extracted by alkylammonium treatment (Mackintosh et al., 1971). Smectite content was estimated from the cation exchange capacity (CEC) measurement. These characterizations were used to improve the reliability of the models by deducing the fitting parameters. The sorption site capacities on sedimentary rock in Horonobe area were, thus, quantified from the Cs sorption isotherms combined with the characterizations of sedimentary rocks.

## 2. Experimental

### 2.1. Materials

The rock samples were obtained from a bore hole named HDB-11 in Horonobe area. The underground near Horonobe Underground Research Center consists of two formations, Koetoi and Wakkanai formation. The sedimentary rock in Horonobe area is considered to be composed of diatom fossils and terrigenous sediments (Yamamoto et al., 2002; Sato, 2003; Hara, 2004). The diatom fossils are gradually crystallized with increasing in depth. The fossils keep their original form in Koetoi formation while the diatom fossils are gradually crystallized to Opal-CT due to the diagenetic effect in Wakkanai formation. In contrast, the property of terrigenous sediments shows no dependency on depth. The terrigenous sediments mainly consist of quartz and plagioclase. A small amount of clay minerals such as smectite, illite and chlorite are detected by XRD analysis. A small amount of siderite, calcite and pyrite are also found as the terrigenous sediments. At the bore hole from which rock samples were obtained, Koetoi formation distributes to 440 m depth. The transition zone ranges from 440 to 465 m. Wakkanai formation is underlying deeper than 465 m. The rock core samples were obtained from the depth of 410, 460 and 590 m of the bore hole. The rock samples were ground into powder of under 150 μm by mortar. The characterization procedures of rock samples will be described in Sections 2.2 and 2.3.

### 2.2. Cation Exchange Capacity (CEC) measurement

To saturate the cation exchange site with $NH_4^+$, the ground powder was dispersed in 1 mol/dm$^3$ $NH_4Cl$ at a solid/liquid ratio 1:10 in a polyethylene centrifuge tube after the ground powder of each rock sample was dried at 110 °C for 24 h. The tubes were shaken for 24 h by a rotary shaker (ATR, Inc. RKVSD). The tubes were centrifuged at 6000 rpm (3900*g*) for 10 min by a centrifugation (Hsiangtai, CN2060) after shaking, and then the supernatant was replaced by a new 1 mol/dm$^3$ $NH_4Cl$ solution. This $NH_4^+$ saturation process was repeated three times. To remove the residual $NH_4Cl$ from the powder, 80% ethanol was added to the tubes. The tubes were centrifuged for 10 min at 6000 rpm and then the supernatant was removed. Washing by 80% ethanol was repeated until $NH_4^+$ concentration could be neglected. After this washing, 0.5 mol/dm$^3$ KCl was added to the tubes at a solid/liquid ratio 1:4. After shaking for 24 h, the tubes were centrifuged for 10 min at 6000 rpm and then the concentration of $NH_4^+$ in the supernatants was measured by a chromatograph (Toso Corporation, 2010). This $NH_4^+$ extraction by KCl was repeated until no $NH_4^+$ was detected. The CECs of samples were calculated from the concentration of $NH_4^+$. CEC measurement was carried out in triplicate for each rock sample.

### 2.3. Potassium extraction by alkylammonium

Micaceous minerals contain non-exchangeable K in the interlayer sites. However, the non-exchangeable cation is known to be extracted by alkylammonium solution under a certain condition (Mackintosh et al., 1971). Therefore, the content of micaceous minerals is considered to be estimated from the amount of K extracted by the alkylammonium treatment considering the structural formula.

The ground powder of each rock was dispersed in 0.1 mol/dm$^3$ dodecylamine solution at a solid/liquid ratio 1:100 in a polyethylene centrifuge tube after the ground powder was dried at 110 °C for 24 h. The tubes were placed in an oven at 70 °C with periodically shaking. The tubes were centrifuged for 10 min at 6000 rpm and then aliquots of supernatant were taken. The concentration of K in the supernatant was measured by ICP-AES (Shimadzu Corporation, ICPS-7500). After three samples were taken with the same procedure, the supernatant was removed and a new 0.1 mol/dm$^3$ dodecylamine solution was added to the tubes. The sampling was repeated three times after the replacement of solution. The 0.1 mol/dm$^3$ dodecylamine solution was prepared from dodecylamine hydrochloride powder (Kanto Chemical co., Inc.).

### 2.4. Sorption experiment

The sorption experiments were carried out by batch method. The ground powder was dispersed in 0.5 mol/dm$^3$ KCl at a solid/liquid ratio 1:100 in a polyethylene centrifuge tube after drying. The tubes were shaken for 24 h, centrifuged at 6000 rpm for 10 min, and then the supernatant was replaced by a new 0.5 mol/dm$^3$ KCl solution. This $K^+$ saturation process was repeated three times. After $K^+$ saturation, 0.01 mol/dm$^3$ KCl was added to the tubes at a solid/liquid ratio 1:150. In order to condition the background electrolyte concentration, 0.01 mol/dm$^3$ KCl solution was replaced three times with shaking and centrifuging. After this conditioning, Cs tracer solution was spiked into the tubes. The initial Cs concentration ranged from $1 \times 10^{-9}$ to $1 \times 10^{-2}$ mol/dm$^3$. The Cs tracer solution for the experiments of initial Cs concentration over $1 \times 10^{-7}$ mol/dm$^3$ was prepared from the nonradioactive CsCl powder (Kanto Chemical co., Inc.). $^{137}$Cs was used as tracer for the experiments of initial Cs concentration of $1 \times 10^{-7}$ mol/dm$^3$ or lower. After spiked, the tubes were shaken for 48 h. The tubes were centrifuged at 6000 rpm for 10 min and 400 μl aliquots of supernatants were taken after shaking. The concentration of nonradioactive Cs was measured by ICP-MS after dilution of the sampled solution by 0.01 mol/dm$^3$ $HNO_3$. The concentration of $^{137}$Cs was measured by γ-ray spectrometry. The samples for the γ-ray spectrometry measurement were prepared by soaking the sampled solutions into filter papers. The experiments in NaCl electrolyte were also carried out using the same procedure as that in KCl described above.

## 3. Results

### 3.1. Characterization of rock samples

The CECs of 410, 460 and 590 m depth samples were determined to be $1.7 \pm 0.1 \times 10^{-4}$, $1.5 \pm 0.1 \times 10^{-4}$ and $1.8 \pm 0.1 \times 10^{-4}$ eq/g, respectively. The amounts of K extracted by alkylammonium treatment were $1.6 \pm 0.1 \times 10^{-4}$, $9.3 \pm 0.1 \times 10^{-5}$ and $5.4 \pm 0.1 \times 10^{-5}$ mol/g for the rock samples of 410, 460 and 590 m depth, respectively. Assuming that the structural formula