

## The Sorption of Selenite onto Ca-Bentonite

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### 1. Introduction

Se-79 has emerged as one of the most frequently considered nuclides in the safety assessments of high-level radioactive waste disposal, especially in the disposal of pyro-process wastes [1], due to its long half life ( $t_{1/2} = 3.0 \times 10^5 \sim 1.1 \times 10^6$  years) [2, 3]. While selenium naturally exists in four different oxidation states, -2, 0, +4 and +6, selenium is likely to exist as -2, 0 and/or +4 in an underground.

In a Korean concept, a canister containing high-level radioactive wastes or spent fuel would be installed in a cylindrical bentonite block placed in a borehole located deep underground. After corrosion of canister, the selenium ions released from waste materials will be contacted with bentonite. In this study, the sorption phenomenon of selenium ion onto bentonite has been examined.

### 2. Experiment

#### 2.1 Reagents

For the sorption test of selenite, a domestic Ca-bentonite was provided from Korean Volclay, and its composition is shown in Table 1. A selenite stock solution was prepared by dissolving  $\text{Na}_2\text{SeO}_3$  (from Aldrich), and it were kept in Teflon<sup>®</sup> bottles. All other reagents used were above pro-analysis grade.

Table 1. Chemical composition of a domestic Ca-bentonite.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O
Wt. %	57.0	20.0	6.2	2.6	0.8	0.9	1.3

#### 2.2 Sorption test

Solution preparation, sorption reaction and sample filtration were performed in an Ar-filled glove box at room temperature. 0.5 g of bentonite was immersed in 10 mL of selenite solutions, respectively. The pH of the solution was then adjusted by adding a small amount of either NaOH or HClO<sub>4</sub> solution. The pH of the solution was adjusted again after shaking for one day.

Selenite can adsorb onto the bentonite in a waste repository. The decrease of selenite concentration by the addition of bentonite can be due to its adsorption onto bentonite and/or the formation of precipitants with the ions released from bentonite. To identify the cause, a

series of washed bentonite was prepared with the following washing procedure: 20 g of bentonite was shaken in 200 mL of DW at the 80 rpm for 2 days, the bentonite solution was then centrifuged at 10,000 rpm for more than 10 minutes. Finally, solid was dried at 50 and 120 °C for 1 day and 3 hours, respectively. Using the same method, bentonite samples washed 2 and 3 times were prepared by rewashing and drying a portion of the bentonite obtained from the previous washing step one after another.

Non-washed bentonite and bentonite washed 1, 2 or 3 times were added into selenite solutions, respectively. After shaking for 7 days, the solutions were filtered by 0.22 μm pore size filter or NMWL 10k ultra-filter. Then, the concentration of selenium in the filtrates was analyzed using ICP-MS.

#### 2.3 Calculation of $K_d$

The amount of selenium sorbed onto bentonite was calculated from the concentration difference between before and after the sorption reaction, and the distribution coefficient ( $K_d$ , mL/g) of selenium was obtained as follows [4]:

$$K_d = \frac{S}{C} = \frac{(C_0 - C)}{C} \cdot \frac{V}{M}$$

where S is the concentration of selenium sorbed onto the unit mass of bentonite (mol/g), C is the concentration of selenium remaining in the solution after sorption reaction (mol/mL),  $C_0$  is the initial concentration of the selenium before sorption reaction (mol/mL), M is the mass of the bentonite (g), and V is the volume of the solution (mL).

### 3. Results and Discussion

The concentration of silicon dissolved from bentonite remained at  $3 \times 10^{-4} \sim 7 \times 10^{-4}$  and  $1.7 \times 10^{-4}$  mol/L in filtrates through a micro-filter and NMWL 10k ultra-filter, respectively. Thus, the concentration of silicon will be below  $1 \times 10^{-3}$  mol/L in neutral and weak alkaline groundwater in a waste repository. After the sorption reaction of selenite onto bentonite, the selenium concentration filtered through the micro-filter was decreased from 0.59 mg/L to 0.45 mg/L after ultrafiltration. These results indicate that few of colloids were formed.

As shown in Fig. 2, the sorption percentage of selenite onto bentonite increased as the concentration of selenite

decreased. While a slight amount of selenite was sorbed in  $10^{-4}$  mol/L of the selenite solution at around pH 9, the sorption amount of selenite reached greater than 50% in  $10^{-6}$  mol/L. Therefore, the sorption of selenite on bentonite cannot be ignored because the selenium concentration will be low in the nuclear waste repository, and a very large quantity of bentonite is used as a buffer material in the waste repository. However, if the selenite concentration is decreased by the formation of a precipitant with soluble cations released from bentonite, the precipitates can barely be formed in the repository since released soluble cations might be flown out during the container life time.

From the sorption test of selenite onto the washed bentonites, a little amount of selenite was still sorbed onto the washed bentonite, while the  $K_d$  values were decreased after first washing. These results indicate that bentonite itself sorbs selenite.

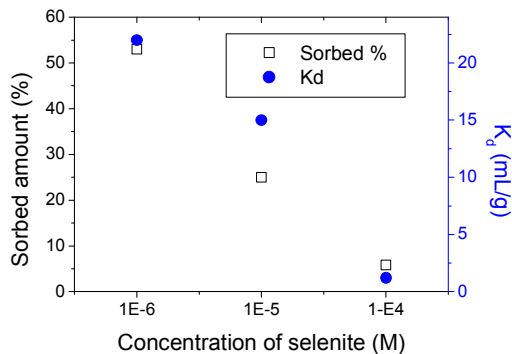


Fig. 1. Sorbed amount(%) and distribution coefficients ( $K_d$ ) of selenite onto unwashed bentonite as a function of selenite concentration at water/bentonite= 20 mL/g and pH= ~ 9.1.

#### 4. Conclusions

In the selenite sorption test onto a domestic Ca-bentonite, the more than half sorption of selenite at low concentration of  $10^{-6}$  mol/L and its sorption onto the washed bentonite suggest that the sorption of selenite by bentonite cannot be ignored in a waste repository.

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