

Selenate Sorption onto Chlorite Surface: Identification of Oxidation State of Selenium Using X-ray Absorption Near Edge Structure (XANES)

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1. Introduction

The long-lived radionuclides ^{79}Se , present in spent nuclear fuel and high-level radioactive waste, is one of elements of concern because of its long half life, which is reported to be 4.8×10^5 or 1.11×10^6 years [1]. Selenium exists in four different oxidation states with very different chemical behaviors such as selenide (Se^{II}), elemental selenium (Se^0), selenite ($\text{Se}^{\text{IV}}\text{O}_3^{2-}$), and selenate ($\text{Se}^{\text{VI}}\text{O}_4^{2-}$) [2]. Clay minerals in engineered barriers and natural barriers such as rocks and aquifer sediments strongly adsorb cationic species, but to lesser extent anions like selenite and selenate. Owing to their negative charge, Se^{VI} and Se^{IV} species adsorb to Fe^{III} oxides, but are only weakly sorbed by clay minerals with prevalent cation exchange capacity [3]. Since Se^{VI} and Se^{IV} oxoanions act as terminal electron acceptors, Se^{VI} and Se^{IV} are reduced abiotically by Fe^{II} -containing solids.

Chlorite is 2:1:1 sheet silicate, commonly green-colored, that occur as a common accessory mineral metamorphic rocks and as an abundant mineral in metamorphic rocks of the chlorite zone. Chlorite is also potentially an important sorbent for radionuclides when radionuclides migrate through fractured crystalline rocks such as granite since it is one of major minerals consisting of the rock fractures. It has been reported that chemical weathering of the chlorite leads to an evolution of altered and newly-formed secondary iron phases as coatings and Fe-colloids [4]. In respect to sorption reactions such secondary phases, in particular iron phases, often dominate the overall sorption behavior of rocks.

Therefore, in this study, we investigated the sorption and the redox reactions of selenate on the chlorite surface using an X-ray Absorption Spectroscopy (XAS) technique, especially X-ray Absorption Near Edge Structure (XANES).

2. Sorption Experiment

2.1 Sorption Experiment

The Fe-rich chlorite used in the experiments was an unaltered ripidolite (CCa-2 chlorite), which was obtained from the Source Clays Repository of the Clay Minerals Society. A chlorite fraction with size of 75-150 μm in diameter was used in the sorption experiments. Sorption experiments were carried out in anoxic condition using a glove-box with an Ar

atmosphere ($\text{O}_2 < 5$ ppm). 0.5 g of chlorite mineral was reacted with 10 mL of solution in 15 mL centrifuge tube. Suspension of chlorite were prepared at two different ionic strengths in NaClO_4 ($I=0.1$ and 0.005 M) and at three different pH values. Selenate as a Na_2SeO_4 was added to achieve a final concentration of 0.01 M. The details of the conditions are given in Table I. Afterward the solid was separated from the liquid by centrifuging twice for 20 min at 7000 rpm. The chlorite was dried under an Ar atmosphere and reserved for XANES measurements.

Table I: Sorption Experimental Conditions

| Samples | Contact time (days) | I (NaClO_4) | pH | Carbonate (NaHCO_3) |
|---------|---------------------|--------------------------|-----|--------------------------------|
| Se-1 | 7 | 0.005 M | 5.0 | 0 |
| Se-2 | 7 | 0.1 M | 4.9 | 0 |
| Se-3 | 20 | 0.1 M | 5.1 | 0 |
| Se-4 | 7 | 0.1 M | 7.5 | 0 |
| Se-5 | 7 | 0.1 M | 8.1 | 0 |
| Se-6 | 7 | 0.1 M | 9.2 | 0 |
| Se-7 | 7 | 0.1 M | 8.5 | 0.01 M |

2.2 XANES Measurements

XANES spectra were collected at the Se K -edge (12,658 eV) at the beamline 3C1 of the PLS (Pohang Light Source, Pohang Accelerator Laboratory). The electron storage ring was operating at 2.5 GeV and beam size is about 0.6 mm in diameter. The energy of the X-ray beam which is operating 2.5-33 keV was tuned by a Si(111) double-crystal monochromator. Two Rh-coated mirrors before and after the monochromator were used to collimate the beam into the monochromator and to reject higher harmonics. Energy calibration was done with 30% detuning and a gain of about 10^7 .

All samples were scanned in fluorescence mode using a 7-element germanium detector with an Ar/ N_2 -filled ionization chamber. An arsenic filter was placed between the sample compartment and the ionization chamber to eliminate elastically scattered X-rays from entering the ionization chamber. Data in the XANES region were collected in steps of 0.2 eV. Fig. 1 shows the arrangement of equipments (b) and its photograph (c) of 3C1 beamline used for XANES measurements.

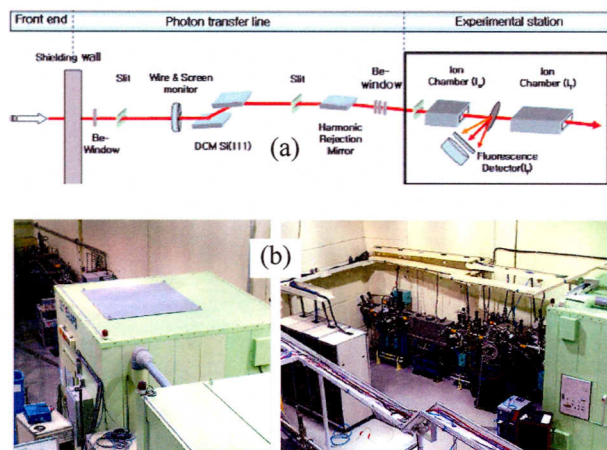


Fig. 1. The arrangement of equipments (a) and its photograph (b) of 3C1 beamline for XANES measurements at PLS.

3. Results and Discussion

3.1 Results of Sorption Experiment

The results of the sorption experiment for XANES measurements were summarized in Table II. Results shows low K_d values regardless of chemical conditions meaning that selenate is nearly sorbed on the chlorite surface. However, K_d values of selenate are relatively decreased as pH and ionic strength increases. As contact time increases from 7 to 20 days, the dissolved Fe ions is reduced, which may mean the re-sorption of the dissolved Fe ions onto chlorite surface while K_d values are not changed. No significant effect of carbonate on the selenate sorption onto chlorite was also observed.

Table II: Result of Sorption Experiment

| Samples | [Se] _{solution} (mg/L) | [Fe] _{dissolved} (mg/L) | % of Sorbed | K_d (mL/g) |
|---------|---------------------------------|----------------------------------|-------------|--------------|
| Se-1 | 927 | 1.33 | 0.96 | 0.19 |
| Se-2 | 889 | 1.80 | 5.02 | 1.00 |
| Se-3 | 886 | 0.59 | 5.34 | 1.07 |
| Se-4 | 912 | 0.43 | 2.56 | 0.51 |
| Se-5 | 916 | 0.24 | 2.14 | 0.43 |
| Se-6 | 923 | 0.31 | 1.39 | 0.28 |
| Se-7 | 915 | 0.33 | 2.24 | 0.45 |

3.2 Result of XANES Measurements

The results of XANES measurements for the samples from Se-1 to Se-8 were shown in Fig. 2. Some standard materials with different oxidation states of selenium were also measured by XANES (solid line in Fig. 2) for the comparison of XANES measurements results of samples.

The results of XANES indicate that selenium sorbed onto chlorite surface remained in oxidation state VI. Therefore, in our system, the selenate do not reduced by the Fe(II) ions present in the surface and/or dissolved from the surface. Since electron transfer from Fe(II) to Se(VI) is strongly favored by heterogeneous surface

reaction, while reduction is restricted in solution, the lack of reduction is most likely due to the inhibited surface reaction [5]. Further investigations should be carried out to explain this coupled reaction of selenium between redox reaction, sorption, and dissolution.

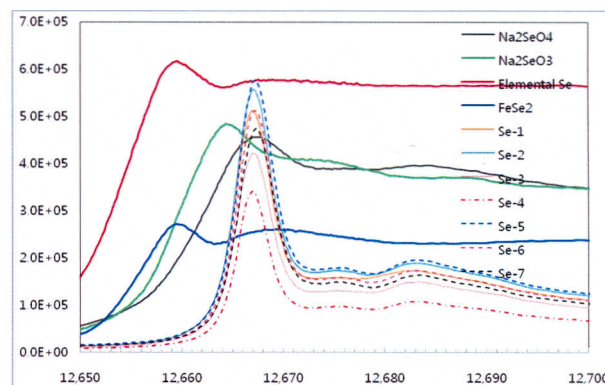


Fig. 2. Results of XANES measurements.

3. Conclusions

In this study, the sorption and the redox reactions of Se^{VI} on the chlorite surface was investigated by using XANES technique. Our experiment is one of a series of experiments prepared for the sorption of Se^{IV} and Se^{VI} onto chlorite. In the future, the heterogeneous redox reaction of selenium coupled with a redox reaction of Fe, dissolution and precipitation of Fe ions, and the effect of Fe(II) ion on the selenium sorption will be further investigated by conducting a series of experiments. In addition, the oxidation states of selenium and sorption mechanism onto chlorite will be studied by using XAS techniques.

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