

## Redox Reactions and Sorption of Selenite (Se<sup>IV</sup>) on Chlorite Surface

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### 1. Introduction

The long-lived radionuclide <sup>79</sup>Se is one of elements of concern because of its long half life ( $4.8 \times 10^5$  or  $1.11 \times 10^6$  years), high mobility, and severe toxicity in the environments. Selenium exists in four different oxidation states with very different chemical behaviors such as selenide (Se<sup>-II</sup>), elemental selenium (Se<sup>0</sup>), selenite (Se<sup>IV</sup>O<sub>3</sub><sup>2-</sup>), and selenate (Se<sup>VI</sup>O<sub>4</sub><sup>2-</sup>). Owing to their negative charge, Se<sup>VI</sup> and Se<sup>IV</sup> species adsorb to Fe<sup>III</sup> oxides, but are only weakly sorbed by clay minerals with prevalent cation exchange capacity [1]. Since Se<sup>VI</sup> and Se<sup>IV</sup> oxoanions act as terminal electron acceptors, Se<sup>VI</sup> and Se<sup>IV</sup> are reduced abiotically by Fe<sup>II</sup>-containing solids.

Therefore, in this study, we investigated the redox reactions and sorption of selenite (Se<sup>IV</sup>) on chlorite mineral which is one of Fe<sup>II</sup>-containing minerals and sorbents for migrating radionuclides. The chemical species of selenium on the chlorite surface was identified using an X-ray Absorption Near-Edge Structure (XANES). In particular, the effects of Fe<sup>II</sup> ions on redox reactions and sorption of selenite on chlorite surface were investigated.

### 2. Sorption Experiment

#### 2.1 Sorption Experiment

The chlorite used in the experiments was an unaltered ripidolite (CCa-2 chlorite) sampled from El Dorado County, California, USA. A chlorite fraction of 75-150  $\mu$ m in diameter was used in the sorption experiments. Sorption experiments were carried out under an anoxic condition using a glove-box with an Ar atmosphere ( $O_2 < 5$  ppm). 0.5 g of chlorite was reacted with 10 mL of solution in a 15 mL centrifuge tube. Suspensions of chlorite were prepared at two different ionic strengths in NaClO<sub>4</sub> ( $I=0.1$  and 0.01 M) and at three different pH values. Selenite as a Na<sub>2</sub>SeO<sub>3</sub> was added to achieve a final concentration of 0.02 M. Details of the conditions are given in Table I.

After a prerequisite contact time, the solid was separated from the liquid using a syringe filter with 0.2  $\mu$ m pore size. Afterwards the chlorite was dried under an Ar atmosphere and reserved for XANES measurements. 50 ppm of ferrous ions (as FeCl<sub>2</sub>) was added to investigate the effects of Fe(II) ions on redox reactions and sorption of selenite on chlorite surface. The concentrations of Fe<sup>II</sup> and Fe<sup>III</sup> in the solution were

measured by a ferrozine method using a UV-VIS spectrophotometer.

Table I: Experimental Conditions for Selenite Sorption

Samples	Contact time (days)	<i>I</i> (NaClO <sub>4</sub> )	pH	Fe(II), ppm (FeCl <sub>2</sub> )
Se-1	7	0.01 M	5.1	-
Se-2	7	0.1 M	5.0	-
Se-3	7	0.1 M	3.3	-
Se-4	7	0.1 M	7.1	-
Se-5	7	0.1 M	9.0	-
Se-6	28	0.1 M	5.0	-
Se-7	56	0.1 M	4.9	-
Se-8	56	0.1 M	5.1	50
Se-9	56	0.1 M	8.9	50

#### 2.2 XANES Measurements

XANES spectra were collected at the Se *K*-edge (12,658 eV) at the 3C1 beamline of the PLS (Pohang Light Source, Pohang Accelerator Laboratory). All samples were scanned in a fluorescence mode using a 7-element germanium detector in the Ar/N<sub>2</sub>-filled ionization chamber. Fig. 1 shows a photograph of the 3C1 beamline at PLS used for XANES measurements.

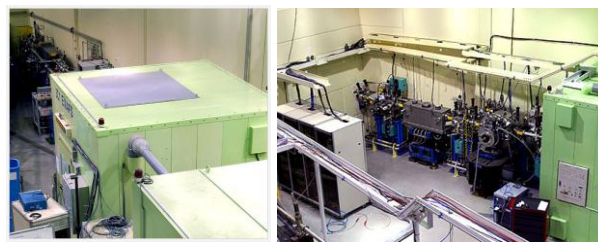


Fig. 1. The arrangement of equipments (a) and a photograph (b) of the 3C1 beamline for XANES measurements at PLS.

### 3. Results and Discussion

#### 3.1 Results of Sorption Experiment

The result of the sorption experiment summarized in Table II shows that the  $K_d$  values of Se<sup>IV</sup> are very low regardless of the chemical conditions and selenite is nearly sorbed on the chlorite surface. When the pH is low (Se-3), the amount of dissolved Fe<sup>II</sup> and Fe<sup>III</sup> ions is increased and a relatively higher  $K_d$  value is obtained. This means that Fe ions were almost not dissolved from the chlorite surface regardless of contact time. Instead, much amount of Mg ions about 10-50 ppm depending

on conditions was dissolved from chlorite surface since the chlorite used contained larger amount of Mg than Fe.

Table II: Result of Sorption Experiment

Samples	[Fe <sup>II</sup> ] (mg/L)	[Fe <sup>III</sup> ] (mg/L)	% of Sorbed	K <sub>d</sub> (mL/g)
Se-1	0.0013	0.0570	0.00	0.00
Se-2	0.0014	0.0804	0.51	0.10
Se-3	0.1664	0.1687	2.91	0.60
Se-4	0.0010	0.0676	1.34	0.27
Se-5	0.0000	0.0827	5.43	1.15
Se-6	0.0155	0.0482	4.03	0.84
Se-7	0.0019	0.0603	4.06	0.85
Se-8	4.8362	0.1882	6.82	1.46
Se-9	0.0000	0.0994	2.03	0.41

When additional 50 ppm of Fe<sup>II</sup> ions are added to the sorption system (Se-8 and Se-9) following three processes can be occurred:

- (P1) formation of precipitating ferrous selenite solid (FeSeO<sub>3</sub>(s)) in the solution
- (P2) oxidation of Fe<sup>II</sup> to Fe<sup>III</sup> by reducing Se<sup>IV</sup> to Se<sup>0</sup> in the solution
- (P3) sorption of Fe<sup>II</sup> ions on the chlorite surface resulting in a heterogeneously reduction of the sorbed Se<sup>VI</sup> to Se<sup>0</sup>

At the alkaline condition (Se-9), almost whole amount of added Fe<sup>II</sup> ions were disappeared. This can implicate that the added Fe<sup>II</sup> ions were sorbed on the chlorite surface or precipitated as a ferrous selenite (FeSeO<sub>3</sub>) or a ferrous selenide (FeSe) solid.

### 3.2 Result of XANES Measurements

The result of XANES measurements for the samples Se-1 to Se-9 is shown in Fig. 2. The XANES result indicates that selenite sorbed onto the chlorite surface is remained in a Se<sup>IV</sup> oxidation state or a Se<sup>VI</sup> depending upon the conditions.

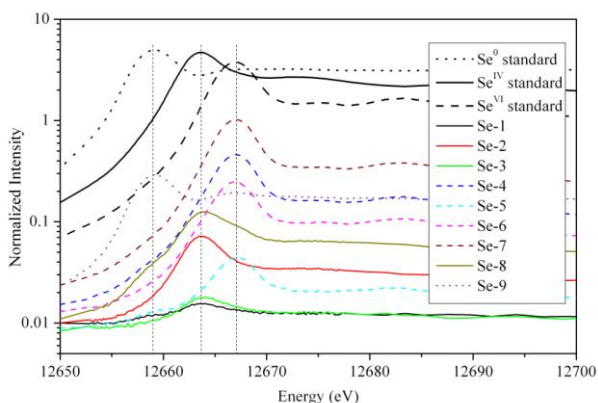


Fig. 2. Results of XANES measurements.

It is interesting to notice that the Se<sup>IV</sup> was oxidized to Se<sup>VI</sup> at a higher pH (Se-4 and Se-5) and contact time

(Se-6 and Se-7). We cannot obviously explain this oxidation of Se<sup>IV</sup> to Se<sup>VI</sup> in a given experimental system. However, it can be presumed that this oxidation may be due to a gradual change of chemical conditions by the dissolution of constituent ions (for instance, Mg<sup>2+</sup>, Al<sup>3+</sup>) from the chlorite surface and/or by some additions of chemical reagents containing oxygen. By the way, some important redox reactions such as the reduction of Se<sup>IV</sup> to Se<sup>II</sup> and the formation of ferrous selenide (Fe<sup>II</sup>Se(s)) were not observed in the XANES measurements.

However, Se<sup>IV</sup> was certainly reduced to elemental selenium (Se<sup>0</sup>) when Fe<sup>II</sup> was added to the system at an alkaline condition (Se-9). This reduction of selenite to elemental selenium is related with the disappearance of the added Fe<sup>II</sup> from the solution as shown in Table II. This disappearance of Fe<sup>II</sup> can be occurred by the sorption of Fe<sup>II</sup> onto the chloride surface. The sorbed Fe<sup>II</sup> can reduce the Se<sup>IV</sup> to Se<sup>0</sup> by the oxidation of Fe<sup>II</sup> to Fe<sup>III</sup>. Thus the peak of Se<sup>0</sup> of the Se-9 sample may be due to the process P3.

On the other hand, Se<sup>IV</sup> was not totally reduced to Se<sup>0</sup> at an acidic condition (Se-8) and only a small peak of Se<sup>0</sup> was appeared at the XANES measurement. The large peak of Se<sup>IV</sup> for the Se-8 sample in the presence of Fe<sup>II</sup> ions may be due to the formation of ferrous selenite solid by the process P1. The possibility for the process P2 was ignored since an electron transfer from Fe<sup>II</sup> to Se<sup>IV</sup> is strongly favored by a heterogeneous surface reaction, while a reduction in the solution is strongly restricted [3].

### 3. Conclusion

In this study, it is noticed that the redox reactions and sorption of selenite are greatly influenced by the presence of Fe<sup>II</sup> ions and pH as well as Eh. Some further studies are necessary to investigate the effects of Fe<sup>II</sup>/Fe<sup>III</sup> ions on heterogeneous surface redox reactions of selenium coupled with aqueous reactions of selenium with iron ions.

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