

# **Spectroscopic study of immobilization mechanism of selenite and selenate in ettringite**

Binglin Guo, Keiko Sasaki

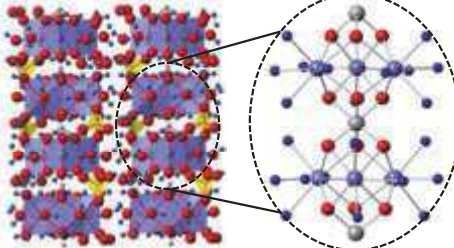
Department of Earth Resource Engineering, Kyushu University, Fukuoka 819-0395, Japan

Ettringite is a crucial cement related material in terms of Se immobilization under alkaline conditions. However, the immobilization mechanisms, atomic configuration, and interchannel structure of Se sorbed in ettringite are unclear. The coordination chemistry of  $\text{SeO}_3^{2-}$  was evaluated through structural insight into ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ) using X-ray diffraction (XRD), Fourier Transform infrared (FTIR) spectroscopies, thermogravimetric analysis (TG), and extended X-ray adsorption fine structure (EXAFS) spectra. It is contrasting between  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$  in chemical property of the solid residues after immobilization. Based on the EXAFS and FTIR analysis, the oxoanion exchange with structural  $\text{SO}_4^{2-}$  is the main mechanism for immobilization of  $\text{SeO}_4^{2-}$ , which is bond by the outer-sphere complex. In contrast,  $\text{SeO}_3^{2-}$  is easily immobilized to form inner-sphere complexes in ettringite. Based on the FTIR and EXAFS results with the bond valence theory, the location sites of sorbed  $\text{SeO}_3^{2-}$  in ettringite structure were also proposed. The results obtained in this work are relevant to the understanding of Se and its isotopes immobilized in cements or alkaline environments, especially for nuclear waste management.

---

### Introduction

**Ettringite:  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$**



- Al
- Ca
- O
- S
- Water

The columns of ettringite are made of  $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}^{6+}$ .  $\text{SO}_4^{2-}$  in intercolumns holds the columns together. Al coordinate with 6 OH and Ca coordinate with 4 OH and 4H<sub>2</sub>O.

**Functional group on the surface**  
 $\equiv\text{Ca}_2\text{-OH}$      $\equiv\text{Al-OH}$      $\equiv\text{Ca-OH}_2$

**Objective**  
 To interpret mechanism in selenite and selenate immobilized in ettringite.

### Materials and Method

**Solutions**  
 ICP-OES (Se, Ca, Al, S) pH

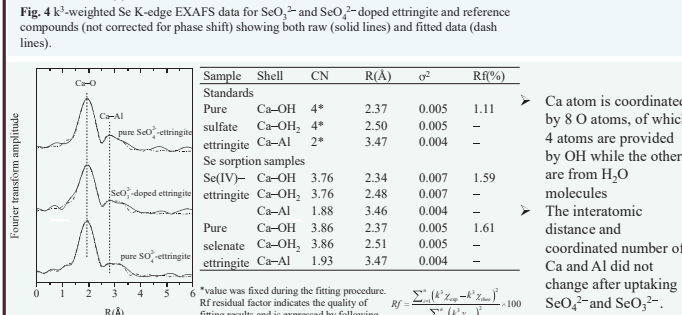
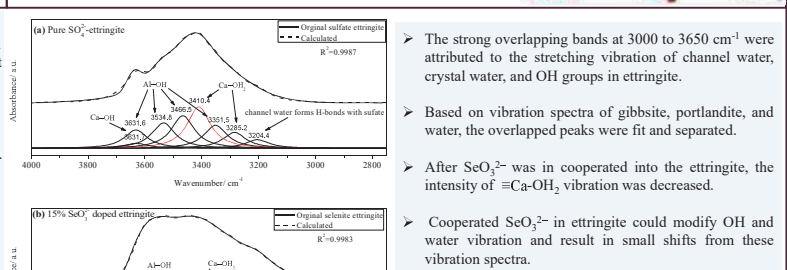
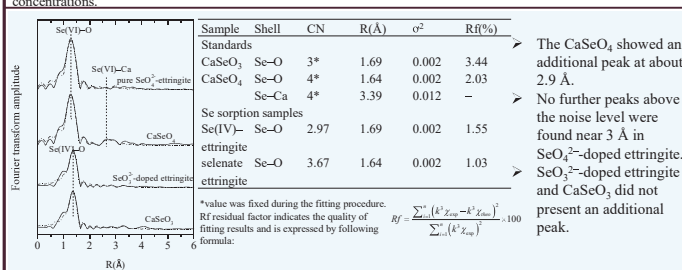
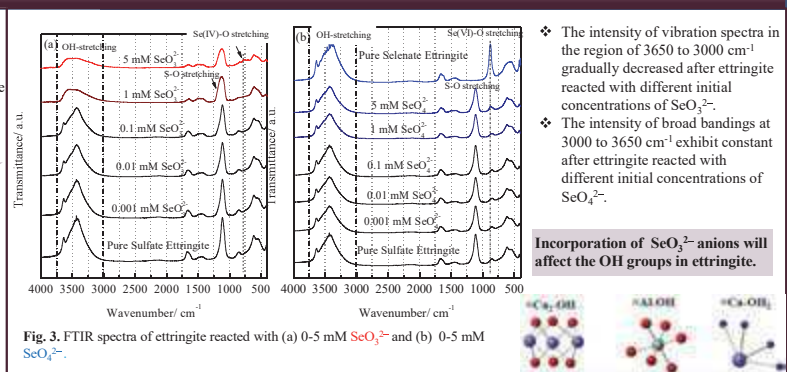
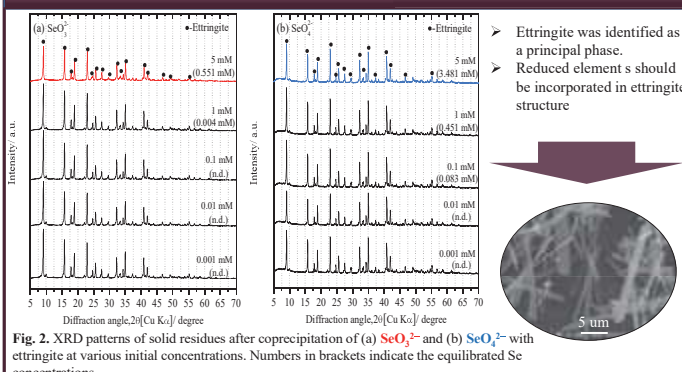
**Stirring**  
 400 rpm  
 120 min

**Filtration**

**Powders**  
 XRD  
 TG-DTA  
 FTIR  
 EXAFS

Ca(OH)<sub>2</sub> 0.445g (60 mmol)  
 0.001–5mM Na<sub>2</sub>SeO<sub>3</sub>  
 10 mM Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Ca:Al=3:1)

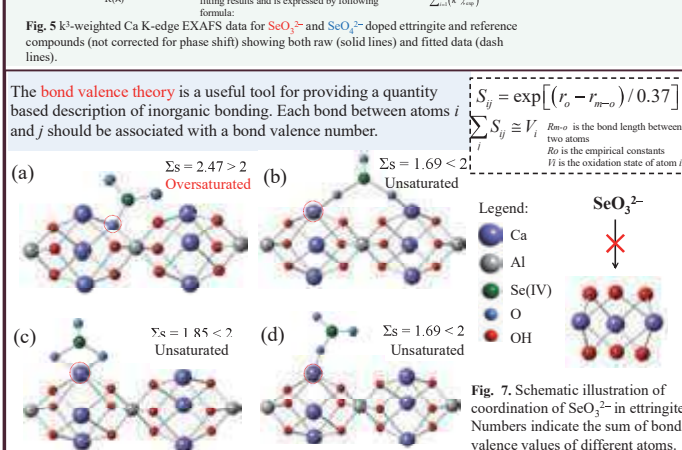
## Results and Discussion



Ettringite was identified as a principal phase.  
 Reduced element s should be incorporated in ettringite structure.

The  $\text{CaSeO}_4$  showed an additional peak at about 2.9 Å.  
 No further peaks above the noise level were found near 3 Å in  $\text{SeO}_3^{2-}$ -doped ettringite.  $\text{SeO}_4^{2-}$ -doped ettringite and  $\text{CaSeO}_4$  did not present an additional peak.

The strong overlapping bands at 3000 to 3650  $\text{cm}^{-1}$  were attributed to the stretching vibration of channel water, crystal water, and OH groups in ettringite.  
 Based on vibration spectra of gibbsite, portlandite, and water, the overlapped peaks were fit and separated.  
 After  $\text{SeO}_3^{2-}$  was in cooperated into the ettringite, the intensity of  $\equiv\text{Ca-OH}_2$  vibration was decreased.  
 Cooperated  $\text{SeO}_3^{2-}$  in ettringite could modify OH and water vibration and result in small shifts from these vibration spectra.  
 The  $\text{SeO}_4^{2-}$  incorporated in ettringite will not change the crystal water, indicating  $\text{SeO}_4^{2-}$  form outer-sphere complex in ettringite.



### Conclusions

- $\text{SeO}_3^{2-}$  is easily immobilized to form inner-sphere complexes with  $\text{Ca-OH}_2$  on the channel edges of ettringite.
- $\text{SeO}_4^{2-}$  is immobilized through outer-sphere complexation via anion exchange with  $\text{SO}_4^{2-}$  in ettringite.
- $\text{SeO}_3^{2-}$  in ettringite is more stable than  $\text{SeO}_4^{2-}$  because inner-sphere complexes are more resistant to remobilization than outer-sphere complexes.
- Based on the surface function groups of ettringite, the potential coordination site was proposed.

Outer-sphere complexation  
 Inner-sphere complexation  
 H<sub>2</sub>O molecules  
 Release