

## COORDINATION CHEMISTRY OF SELENATE IN ETTRINGITE

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### Introduction

Selenium often occurs in association with sulfide minerals by replacement with sulfur, and its toxicity is known as being associated with a number of specific diseases such as nail abnormalities and changes in peripheral nerves. Selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ) are much more mobile and toxic in ecosystems. Furthermore, the high mobility of radionuclide  $^{79}\text{Se}$  in aqueous environments can pose the terrible threat because most minerals' surfaces are negatively charged in earth crust and it has a long half life time around  $2.95 \times 10^5$  years.

Ettringite, which is one of calcium aluminum hydroxysulfates with several crystal water molecules, often occurs in some alkaline environments like cements. It has a general composition of  $\text{A}_6\text{B}_2(\text{C})_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ , where A is  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$ ; B is  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{4+}$ ,  $\text{Si}^{4+}$ ; and C is some anions such as  $\text{SO}_4^{2-}$  and  $\text{SeO}_4^{2-}$  (Gougar et al., 1996). The unit cell of the crystal consists of columns of  $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}^{6+}$  with the inter-column spaces occupied by 3 moles of divalent anions (C) and 2 moles of  $\text{H}_2\text{O}$ , which hold columns together through electrostatic force. It has been proved by the bond valence theory that  $\text{AsO}_4^{3-}$  is complexed with some functional groups on the surface of columns in ettringite (Myneni et al., 1998). Thus, there are two possibilities in incorporations of oxoanions in ettringite, which are the substitution of intercolumn oxoanions or the coordination of oxoanions with functional group on ettringite. This should affect to the chemical stability of anionic species, which are sometimes pollutants in ettringite.

It is not yet clear whether  $\text{SeO}_4^{2-}$  is sorbed through inner-sphere complexation or outer-sphere complexation in ettringite. In other word, the bonding  $\text{Ca}(\text{Al})\text{-O-Se-O}_3$  should be created through covalent bond while the bonding  $\text{H} \cdots \text{O-Se-O}_3$  should be formed in the later through electrostatic force. In the present work, ettringite containing different concentrations of selenate was characterized by Fourier Transform infrared spectroscopy (FTIR) and bond valence theory to figure out the sorption mechanism of selenate in ettringite.

### Methods

Ettringite was synthesized with the stoichiometric amounts of  $\text{Ca}(\text{OH})_2$  and  $\text{Al}_2(\text{SO}_4)_3$  with different concentrations of  $\text{Na}_2\text{SeO}_4$  (0.5–20mM) in ultrapure water. All solutions were prepared by deionized water and reagent-grade chemicals. The mixture were covered with parafilm to avoid getting  $\text{CO}_2$  and stirred using a magnetic stirrer at room temperature for 120 min. Then the pH of supernatant was recorded and suspension was filtered by membrane filter for determination of remaining Ca, Al, Se and S concentrations using inductively coupled plasma optical emission spectrometry (ICP-OES). The precipitates were examined by using scanning electron microscope (SEM), X-ray diffraction (XRD), and FTIR. Bond valence theory (Brown et al., 1985) was also applied to calculate the coordination numbers of O atoms in  $\text{SeO}_4^{2-}$  surface functional groups of ettringite.

## Results

Changes of water chemistry during immobilization of  $\text{SeO}_4^{2-}$  in ettringite were monitored until the equilibrium by determination using ICP-OES. Based on the results of XRD for the solid residues, there is no other phases than ettringite with increase in  $\text{SeO}_4^{2-}$  concentrations. Moreover, SEM image has shown needle-like crystals, which are characteristic to ettringite. These results suggest that immobilized  $\text{SeO}_4^{2-}$  were completely substituted into inter column spaces in ettringite structure. Furthermore, as shown XRD results, with increasing the amount of immobilized  $\text{SeO}_4^{2-}$  in ettringite, the cell parameters  $a$  and  $c$  also increased.

In ettringite, there are several types of  $-\text{OH}$  groups including  $\equiv\text{Ca}-\text{OH}_2$ ,  $\equiv\text{Al}-\text{OH}$  and  $\equiv\text{Ca}_2-\text{OH}$ , which produce board FTIR peaks to assign to the stretching vibration mode of O-H around 3200 to 3560  $\text{cm}^{-1}$ . Incorporation of  $\text{SeO}_4^{2-}$  into the columns of ettringite perturbed the  $-\text{OH}$  stretching vibration. With increasing the amount of immobilized  $\text{SeO}_4^{2-}$  in ettringite, the intensities of  $-\text{OH}$  stretching peaks decreased in the range of 3250 to 3400  $\text{cm}^{-1}$  which is assigned to the  $-\text{OH}$  stretching vibration of  $\equiv\text{Ca}-\text{OH}_2$ . This indicates that  $\text{SeO}_4^{2-}$  interacted with  $\text{H}_2\text{O}$  which is coordinated to Ca. Based on the structure of ettringite,  $\equiv\text{Ca}-\text{OH}_2$ ,  $\equiv\text{Al}-\text{OH}$  and  $\equiv\text{Ca}_2-\text{OH}$  sites are arranged in the column surfaces, where  $\equiv\text{Ca}-\text{OH}_2$  is the most dominant sites. According to the bond valence theory, Se-O has 1.62 valence units (v.u.) and O-H does about 0.78 v.u. Ligand exchange to such as  $\equiv\text{Ca}-\text{OH}-\text{SeO}_3$  does not happen, because Se-O-H bond has been already saturated (Brown et al., 1985). Similar characteristic of  $\text{AsO}_4^{3-}$  has been also demonstrated (Myneni et al., 1998). In ettringite,  $\text{SeO}_4^{2-}$  can be only interacted with these function groups through the formation of inner-sphere complexes of  $\equiv\text{Ca}-\text{O}-\text{SeO}_3$ . It is supposed that the significant change in  $-\text{OH}$  vibrations may result from the  $\text{SeO}_4^{2-}$  sorption in ettringite and the formation of inner-sphere complexes.

## Conclusions

The ettringite shows promising application in immobilization of large concentrations of  $\text{SeO}_4^{2-}$  in aqueous environments. In the present work, the mechanism of  $\text{SeO}_4^{2-}$  by co-precipitation with ettringite was discussed. According to the FTIR spectra, the peak intensity in  $-\text{OH}$  stretching mode vibration significantly decreased with increasing the amount of immobilized  $\text{SeO}_4^{2-}$  in ettringite. Furthermore, based on the XRD patterns, sorption of  $\text{SeO}_4^{2-}$  increased the cell parameters  $a$  and  $c$  of ettringite. EXAFS and TG-DTA analysis would exemplify this assumption.

## References

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