



Selenite and selenate uptaken in ettringite: Immobilization mechanisms, coordination chemistry, and insights from structure



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ABSTRACT

Although ettringite is a crucial material in terms of Se immobilization, the immobilization mechanisms, atomic configuration, and intercolumn structure of Se sorbed in ettringite are unclear. The immobilization mechanism of Se oxoanions was evaluated through structural insight into ettringite. It is contrasting between SeO_3^{2-} and SeO_4^{2-} in chemical property of the solid residues after immobilization. The oxoanion exchange with structural SO_4^{2-} is the main mechanism for immobilization of SeO_4^{2-} . In contrast, SeO_3^{2-} is easily immobilized to form inner-sphere complexes in ettringite. In addition, it is necessary to reveal the SeO_3^{2-} complexation sites for understanding the mechanisms in immobilization of SeO_3^{2-} . Based on the characterization results with the bond valence theory, the location sites of sorbed SeO_3^{2-} in ettringite structure were proposed. The results obtained in this work are relevant to the understanding of Se and its isotopes immobilized in cement or alkaline environments, especially for nuclear waste management.

1. Introduction

Selenium (Se) is one of the important micronutrients for human and animal health. At high concentrations, however, selenium toxicity is recognized as a severe environmental and health hazard, because it is toxic to organs. Such an element is existed in nature as selenide minerals and is often associated with sulfide minerals by the substitution of sulfur. Some anthropogenic activity such as various mining and oil refinery activities can cause high concentrations of Se in the effluent (170–6000 $\mu\text{g/L}$) [1,2]; this could result in Se entering the environment and hydrosphere. In addition, the ^{79}Se isotope as one kind of radioactive contamination is a continuing concern surrounding activities related nuclear waste disposal, reprocessing, and nuclear accidents [3]. It has a long half-life time of approximately 3.27×10^5 years with high mobility in the environment [4]. Because of its high toxicity, the WHO and U.S. established the primary drinking water standard as 0.01 mg/L of selenium [5,6]. Therefore, the removal of Se from aqueous environments is urgently required.

The reduced forms of selenium (Se^{2-}) are mainly immobilized in ores, whereas the oxidized forms (SeO_3^{2-} and SeO_4^{2-}) represent the much more mobile and toxic species in water and soil systems. The pyramidal oxoanion SeO_3^{2-} can exist as H_2SeO_3 or HSeO_3^- depending on the pH of the solution ($\text{p}K_{a1} = 2.64$ and $\text{p}K_{a2} = 8.4$) [6,7]. The tetrahedral oxoanion SeO_4^{2-} behaves as HSeO_4^- with a $\text{p}K_a = 1.7$ [7]. The interactions of these oxoanions with mineral surfaces affect their

solubility and mobility. It has been proven that iron and aluminum oxide minerals and coatings are the most common geosorbents for Se oxoanions due to their relatively high point of zero charge with 6–9.5 [8–10]. However, under high pH conditions, both oxidized forms show a lower adsorption capacity because of the negatively charged surface of most minerals.

Ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) forms in the natural alkaline environment, associated with other species like portlandite, gypsum or afwillite [11], and also occurs as the early hydration product of Portland cement generated by hydration [12,13]. Furthermore, Portland cement is an important material for the immobilization and storage of various hazardous material and ettringite is assumed to play an important role in immobilization process. Because of high ion exchange ability, many researchers [14–17] have investigated incorporating the oxoanion of Se by substituting SO_4^{2-} in ettringite. Some of them also indicated that more efficient immobilization of SeO_3^{2-} than that of SeO_4^{2-} occurred through the formation of SeO_3^{2-} -substituted ettringite [18]. However, the reasons for the difference in immobilization efficiency of these oxoanions and intercolumn structure changing of ettringite after sorption these oxoanions are still unclear.

Based on the previously reported structure model of ettringite [19,20], the unit cell of ettringite consists of columnar $\{\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}\}^{6+}$. In columns, 6 coordinated octahedral $\text{Al}(\text{OH})_6^{3-}$ is linked to 3 neighbors Ca atoms. Each Ca atom is eight coordinated (square antiprismatic geometry) by 4 H_2O and 4 OH^- ions, which

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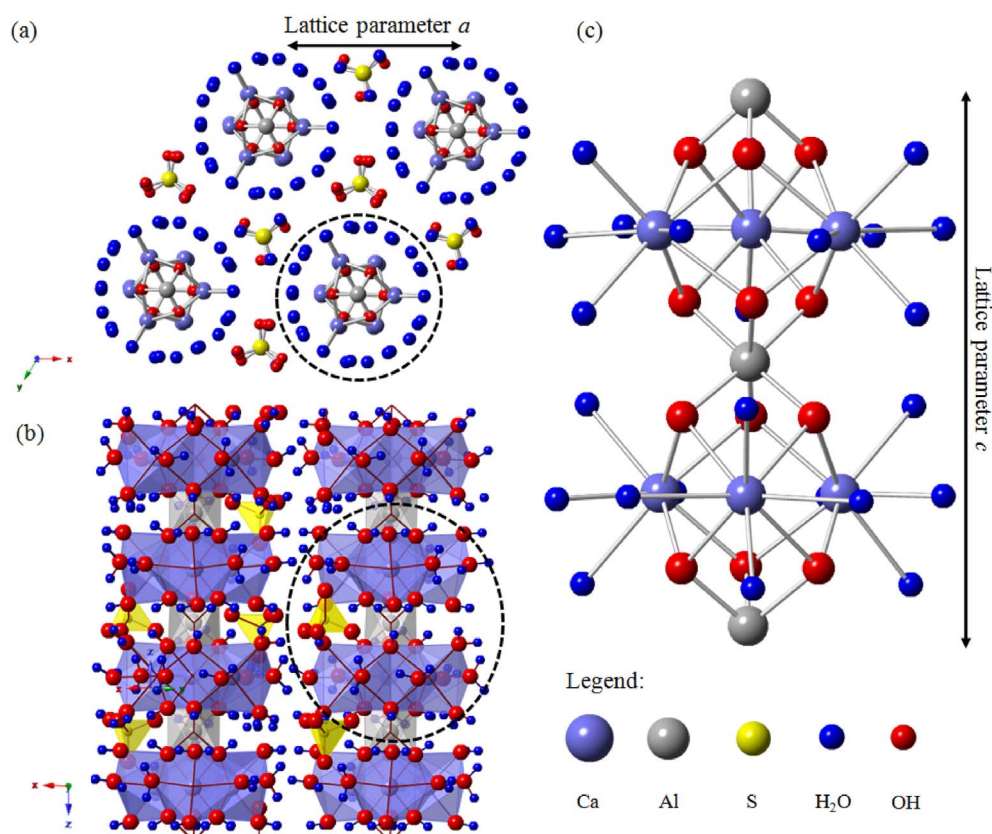


Fig. 1. Structure of ettringite. (a) Perpendicular to c-axis shown columns and channels, (b) projection of ettringite structure, (c) expanded the dash line regions in (a) and (b) [1,2].

means $\text{Al}(\text{OH})_6^{3-}$ octahedra and Ca-O_8 square antiprismatic polyhedra share OH^- ions. The inter-column spaces are occupied by H_2O molecules and SO_4^{2-} ions. This holds the columns together through electrostatic force, as described in Fig. 1. Ettringite is particularly well known as an anion-exchanger [15–17,21–24], and the anions are commonly immobilized through substitution for sulfate in ettringite [15]. In addition, arsenate (AsO_4^{3-}) sorbed in ettringite could cause the formation of inner-sphere complexes with some functional groups on the ettringite channels [25,29]. Therefore, the immobilization of oxoanions by ettringite is due to the substitution with inter-column oxoanions (SO_4^{2-}) or formation of complexes with the channel edge functional groups ($\equiv\text{X-OH}$ and $\equiv\text{X-OH}_2$).

Ettringite is a crucial material in terms of SeO_3^{2-} and SeO_4^{2-} immobilization under alkaline conditions [26]; however, the immobilization mechanism of these oxoanions has not yet been well interpreted, and atomic configuration is needed to consider on the columnar parts edges of SeO_4^{2-} and SeO_3^{2-} sorbed on this mineral. Thus, to understand the SeO_3^{2-} and SeO_4^{2-} immobilization by ettringite in alkaline environments, revealing the mechanism of SeO_4^{2-} and SeO_3^{2-} immobilization in ettringite is necessary for the purpose of environmental remediation and nuclear wastes treatment. In this study, the coordination chemistry of SeO_4^{2-} and SeO_3^{2-} was discussed and the mechanism of these oxoanions' immobilization through co-precipitation with ettringite was elaborated systematically. The combination of extended X-ray adsorption fine structure (EXAFS), thermogravimetric analysis (TG), and Fourier Transform Infrared (FTIR) results, the bond length of atoms, and the detailed analysis of FTIR vibration mode in hydroxyl groups provides evidence to evaluate the coordination chemistry of SeO_3^{2-} in the ettringite.

2. Experimental

2.1. Sample preparation

A series of SeO_4^{2-} and SeO_3^{2-} doped ettringite was synthesized through coprecipitation: 100 ml aqueous solutions containing 10 mM $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and 0.001–5 mM Na_2SeO_4 or Na_2SeO_3 . 0.445 g of powdery $\text{Ca}(\text{OH})_2$ was introduced into 100 ml of the above solutions to obtain a theoretical (3:1) molar ratio of Ca: Al in ettringite. The mixtures were subsequently covered with parafilm to avoid CO_2 contamination and then thoroughly mixed using a magnetic stirrer for 24 h at room temperature. After that, suspensions were taken and filtered through a 0.2 μm membrane filter (Advantec, Japan) to provide the solutions for determining the residual Ca, Al, S, and Se concentrations by using inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer, Optima 8300, US). Separately, SeO_4^{2-} could be totally substituted with sulfate [27], the pure SeO_4^{2-} -substituted ettringite was applied to be the typical SeO_4^{2-} doped ettringite for analysis. The precipitates were dried in silica gel in desiccators under mild vacuum conditions for one week to remove excess water. Moreover, the synthesized SeO_3 and SeO_4 -doped ettringite were dissolved by 0.5 M HNO_3 and the elements were measured by ICP-OES. Based on the water chemistry, the chemical composition of SeO_3 and SeO_4 -doped ettringite were determined. In addition, the crystal water of ettringite was determined by TG analysis.

2.2. Characterization of solid residues

After precipitation, solid residues were characterized using powder X-ray diffraction patterns on an Ultima IV (RIGAKU, Akishima, Japan) using $\text{Cu K}\alpha$ radiation (40 kV, 40 mA) at a scanning speed of 2°min^{-1} and a scanning step of 0.02° . In addition, using the Miller indices reported on ICDD PDF Card (# 042-0224 and # 041-1451), the d spacings from the XRD analyses of the subjected solid residues, and the equation

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