Spectroscopic study of immobilization mechanism of selenite and selenate in ettringite

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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 SeO₃²⁻ was evaluated through structural insight into ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) 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 SeO₃²⁻ and SeO₄²⁻ in chemical property of the solid residues after immobilization. Based on the EXAFS and FTIR analysis, the oxoanion exchange with structural SO₄²⁻ is the main mechanism for immobilization of SeO₄²⁻, which is bond by the outer-sphere complex. In contrast, SeO₃²⁻ 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 SeO₃²⁻ 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.

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Introduction **Materials and Method** The columns of ettringite are made of Ettringite: Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O 0.445g (60 mmol) ${Ca_6[Al(OH)_6]_2 \cdot 24H_2O]}^{6+}$ Solutions (Se, Ca, Al, S) SO₄²⁻ in intercolums holds the columns together. 0.001~5mM Na,SeO, Al coordinate with 6 OH and Ca coordinate 10 mM Al₂ (SO₄)₃ with 4 OH and 4H₂O. (Ca:Al=3:1) Functional group on the surface ≡Ca₂-OH ≡Al-OH ≡Ca₂-OH Stirring | 120 min XRD TG-DTA **Objective** Water Powder FTIR To interpret mechanism in selenite and EXAFS with a single column showing Al polyhedra and Ca polyhedra selenate immobilized in ettringite.

Results and Discussion Ettringite was identified as a principal phase. Reduced element s should be incorporated in ettringit (n.d.) (n.d.) angle 26[Cu Ka]/ de Diffraction ngle,20 Cu Kal/degr

R(Å)

1.64

1.64

0.002 0.012

0.002 1.55

Rf(%)

1.03

2.9 Å.

present an additional

es after coprecipitation of (a) SeO₃²⁻ and (b) SeO₄²⁻ ettringite at various initial concentrations. Numbers in brackets indicate the equilibrated Se

Se-Ca

2.97 1.69

Sample Shell

Se(IV)- Se-O

selenate Se-O

CaSeO.

CaSeO₄

ettringite

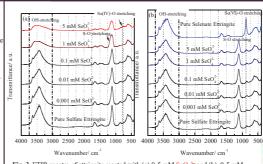
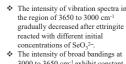
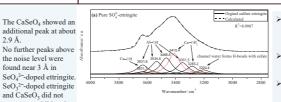


Fig. 3. FTIR spectra of ettringite reacted with (a) 0-5 mM SeO₃²⁻ and (b) 0-5 mM



3000 to 3650 cm⁻¹ exhibit constant after ettringite reacted with different initial concentrations of SeO₄2-

Incorporation of SeO32- anions will affect the OH groups in ettringite.



The strong overlapping bands at 3000 to 3650 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 SeO32- was in cooperated into the ettringite, the intensity of \equiv Ca-OH₂ vibration was decreased.
- Cooperated SeO₃²⁻ in ettringite could modify OH and water vibration and result in small shifts from these vibration spectra.
- The $\mathrm{SeO_4^{2-}}$ incorporated in ettringite will not change the crystal water, indicating SeO₄²⁻ form outer-sphere complex in ettringite

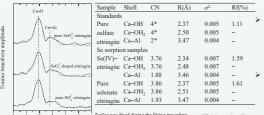
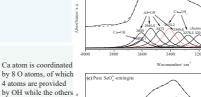


Fig. 4 k³-weighted Se K-edge EXAFS data for SeO₃²⁻ and SeO₄²⁻ doped ettringite and reference compounds (not corrected for phase shift) showing both raw (solid lines) and fitted data (dash

Fig. 5 k3-weighted Ca K-edge EXAFS data for SeO₃2 and SeO₄2 doped ettringite and referencempounds (not corrected for phase shift) showing both raw (solid lines) and fitted data (dash lines).



are from H₂O molecules The interate distance and coordinated number of Ca and Al did not change after uptaking SeO₄²-and SeO₃²-

Numbers indicate the sum of bond

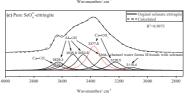
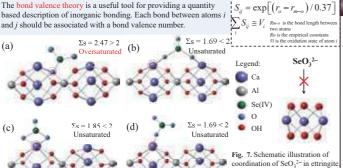


Fig. 6. Curve fitted FTIR spectra in the 2750~4000 cm⁻¹ region for (a) pure sulfate ettringite; (b) 15% selenite-doped ettring (c) pure selenate ettringite



- SeO₃²⁻ has high possibility to react with surface function groups and remove coordinated water
- SeO₃²⁻ forms inner-sphere complexes with surface function groups in ettringite.
- SeO₄²- just can forms outer-sphere complexes with surface function groups in ettringite.



- SeO₃²⁻is easily immobilized to form inner-sphere complexes with Ca-OH2 on the channel edges of ettringite. SeO₄²⁻ is immobilized through outersphere complexation via anion exchange
- with SO₄²⁻ in ettringite SeO₃²⁻ in ettringite is more stable than
- SeO₄²⁻ 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.

