

## Environmental impact of amino acids on the stability of layered double hydroxides after immobilized selenate and iodide

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### 論 文 内 容 の 要 旨

Selenium-79 ( $^{79}\text{Se}$ ) as one of the radioactive isotopes of selenium (Se) with a  $3.27 \times 10^5$  years of half-life. In aqueous environments, Se species behave as anionic species, which can be immobilized in layered double hydroxides (LDHs). Soil organic matter (SOM) is known to be a risk to affect the stability of minerals in pedosphere where low-level radioactive wastes are buried. If the radioactive wastes are released into the soil environment from cementitious materials during a long-term storage, the adsorbed radionuclides might be possibly contacted with SOM. However, the releasing behaviors of  $\text{SeO}_4^{2-}$  and  $\text{I}^-$  from LDHs are still unclear, but important to evaluate its effectiveness. Five amino acids were selected as the model of SOM to investigate the environmental impact.

First **Chapter 1** overviewed the background information of low-level radionuclides, occurrence and characteristics of SOM including its relation with amino acids, characteristics of Se and I anionic species, and their immobilization is overviewed, where LDHs are the key matrix for removal of anionic species as well as byproducts in the aging of cement. The reason why five amino acids were selected as simplified models to represent the environmental factors here was also described. The density of functional theory (DFT) calculation is an important approach in the present work to simulate the stable configurations of ion-exchanged amino acids in LDHs.

All the methodology in the present work was introduced in **Chapter 2**, including the solution analysis (induced coupled plasma-optical emission spectrometry, induced coupled plasma-mass spectrometry, ion chromatography, high-performance liquid chromatography), solid characterization (X-ray diffraction pattern (XRD), X-ray fluorescence spectrometry, scanning electron microscopy, and CHN analysis) and DFT simulation.

In **Chapter 3**, iodide-bearing hydrocalumite ( $\text{Ca}_2\text{Al-LDH(I)}$ ) was synthesized through co-precipitation.  $\text{Ca}_2\text{Al-LDH(I)}$  was very fragile compared with  $\text{Ca}_2\text{Al-LDH(SeO}_4)$  and  $\text{Mg}_2\text{Al-LDH(SeO}_4)$ , which are discussed in subsequent chapters. It is probably due to a small charge and hydrophobicity of  $\text{I}^-$ . Cysteine ( $\text{H}_2\text{Cys}$ ) and aspartic acid ( $\text{H}_2\text{Asp}$ ) accelerated the release of  $\text{I}^-$  from  $\text{Ca}_2\text{Al-LDH(I)}$  than other amino acids.  $\text{H}_2\text{Cys}$  caused ion exchange with  $\text{I}^-$  on hydrocalumite more preferentially than  $\text{H}_2\text{Asp}$ . The intercalation of  $\text{Cys}^{2-}$  was evidenced by XRD of the solid residues, which was supported by DFT calculation predicting the interaction force is ascribed to the hydrogen and Ca-O chemical bonds between carboxyl groups in amino acid and metallic hydroxide layers in LDH.

Next, the more stable LDH, selenate-bearing hydrotalcite ( $\text{Mg}_2\text{Al-LDH(SeO}_4)$ ) was synthesized to

examine the effect of amino acids (**Chapter 4**). Glycine (HGly), H<sub>2</sub>Cys, and H<sub>2</sub>Asp showed intercalation, causing to release of SeO<sub>4</sub><sup>2-</sup>, while tryptophan (HTrp) and phenylalanine (HPhe) did not. Clear differences were verified by solution data as well as XRD, which resulted from several factors including ionic sizes, hydrophilicity, and charge numbers of amino acids. DFT simulation well demonstrated a layer spacing value caused by singly stacked HGly molecule, and the layer spacings of the main and shoulder peaks caused by doubly stacked HGly molecules. Specific interaction of Cys with Mg was also predicted through the thiol group in Cys, which explained the experimental results clearly suppressing Mg<sup>2+</sup> dissolved.

To get closer to a more realistic system, selenate-bearing hydrocalumite (Ca<sub>2</sub>Al-LDH(SeO<sub>4</sub>)) was prepared and investigated in **Chapter 5**. With the increase in the loading amounts of amino acids on Ca<sub>2</sub>Al-LDH, the release of SeO<sub>4</sub><sup>2-</sup> increased in the presence of HGly, H<sub>2</sub>Asp, and H<sub>2</sub>Cys, but not in HPhe and HTrp series. DFT simulation exemplified that Asp<sup>2-</sup> in the interlayer of Ca<sub>2</sub>Al-LDH has several possible configurations, and the stability of SeO<sub>4</sub><sup>2-</sup> in LDH is more strongly affected by CO<sub>3</sub><sup>2-</sup> in hydrocalumite, compared with hydrotalcite.

As an analogical model of the realistic matrix that stabilizes selenate, the fly ash blended cement was supplied for the leaching test in the presence of amino acids in **Chapter 6**. During the aging period, anionic exchangers such as hydrocalumite and ettringite were produced in the cement. H<sub>2</sub>Asp and H<sub>2</sub>Cys enhanced the dissolution of selenate because of ion exchange on hydrocalumite. Other anionic pollutant species from fly ash such as arsenate, chromate, borate, and fluoride did not exceed the environmental standard except for selenate, indicating Se oxoanions are difficult species to immobilize.

So one measure was tried to stabilize Se oxoanions by mixing zero-valent iron (ZVI) with the fly ash cement in **Chapter 7**. Under the present condition, Se oxoanions were not effectively stabilized probably because ZVI was spent for reduction of coexisting Cr(VI) and As(V) species, which have the higher standard redox potentials. It can be predicted that Se(VI)/Se(IV) oxoanions can be reductively immobilized on ZVI in the absence of competing species.

Finally, the main conclusion of the thesis was summarized in **Chapter 8**. The environmental impact of amino acids on the stability of selenate and iodide in LDHs was investigated in experimental and the DFT approaches. Smaller-sized amino acids have a more serious risk to unstabilize selenate and iodide. Carbonate is also another environmentally important threatening factor to the stability of selenate. The necessity of engineering measures to improve the stability of selenate was emphasized.