

Immobilization of selenium and iodine as radionuclide surrogates in cement related materials for burying after solidification

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論 文 名 : Immobilization of selenium and iodine as radionuclide surrogates in cement related materials for burying after solidification
(放射性セレンおよびヨウ素のセメント関連材料中への埋設に向けた固定化に関する研究)

区 分 : 甲

論 文 内 容 の 要 旨

The confinement of radionuclides or hazardous elements is an important issue for preventing environmental contamination and helping to maintain safe ecosystems for living organisms. Among the radioactive isotopes, the ^{129}I and ^{79}Se isotope are considered as remarkable environmental risk related to nuclear waste storage or disposal because of their relatively long half-life (1.57×10^7 years and 2.95×10^5 , respectively) and high mobility in soil and aqueous system. Since radioactive isotopes are a relatively emergent contaminant and nuclear wastes are usually immobilized in cement, immobilization of I and Se species to cementitious materials is of great interest. As a major and active component in hydrated cement, ettringite is assumed to play a role in immobilization of toxic anions because of its ion-exchange ability. This thesis investigated the immobilization mechanisms and properties of iodine and selenium as radionuclide surrogates in ettringite. In addition, the stability of ettringite after uptake toxic anions is also discussed. After accumulation of radionuclides from a contaminated source, ettringite should be stabilized before landfilling for long time storage. An investigation into developing the alternative method to stabilize hazardous wastes by using industrial byproduct/wastes to synthesis glass-ceramics is also conducted.

In **Chapter 1**, the background information of selenium and iodine, including the history, property, toxicity of these elements, as well as their radionuclide isotopes property was elucidated. The characteristic of ettringite and its related minerals are also presented. Based on the presented background, the purpose and motivations of this thesis were discussed.

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. In **Chapter 2**, 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.

In **Chapter 3**, the effect of SO_4^{2-} on SeO_4^{2-} immobilization was investigated, because SO_4^{2-} is one of the major ions in aqueous and soil environments and it is easily incorporated in ettringite. The formation

mechanisms of SeO_4^{2-} -substituted ettringite with and without SO_4^{2-} were systemically elucidated. When SO_4^{2-} and SeO_4^{2-} coexisted, both oxoanions were immediately coprecipitated with ettringite after adding a Ca source. Although SO_4^{2-} was partially substituted by SeO_4^{2-} in ettringite, no other phases were formed during the process. Without SO_4^{2-} , SeO_4^{2-} -substituted hydrocalumite was formed as an intermediate, confirmed by X-ray diffraction peak at d 2.878 Å, as well as by scanning electron microscopy with energy dispersive X-ray spectroscopy and zeta potential measurements. It is clear that the incorporation mechanism of SeO_4^{2-} in ettringite is dependent on coexisting SO_4^{2-} in aqueous environments.

Understanding of immobilization mechanisms of I^- and IO_3^- in ettringite is particularly important in hazardous and radioactive waste management. In **Chapter 4**, the immobilization performance of I^- and IO_3^- in ettringite is discussed. I^- is difficult to be incorporated in ettringite structure. Meanwhile IO_3^- exhibits high affinity to be incorporated in ettringite through hydrogen bond and electrostatic force via anion exchange with SO_4^{2-} . In order to figure out the immobilization mechanism of I^- and IO_3^- via ettringite, various anions with different ionic radius and valence were compared to co-precipitate with ettringite. According to the different anions' properties and the structure of ettringite, the immobilization mechanism of various anions via ettringite is finally proved to relate to the subjected anions' hydration ability and ionic radius.

In **Chapter 5**, the chemical stability of ettringite, which has uptaken toxic anions, were evaluate under the aqueous solution. After coprecipitation, selenate ettringite was formed. However, when this mineral was soaked in a sulfate solution, the destructuralization was observed. In addition, the columnar structure of the destructuralized ettringite was maintained as confirmed via its characterization by a variety of techniques. The destructuralization will cause the immobilized toxic anions re-diffused. The pure ettringite is not ideal as the final product to accommodate hazardous ions.

In general, to reduce the volume of bulky sludge after co-precipitation, heat treatment is applied. In **Chapter 6**, the thermal stability of SeO_4^{2-} bearing ettringite was investigated. SeO_4^{2-} bearing ettringite was gradually transformed to a new crystal phase until 600 °C, which should be assigned to $6\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SeO}_2$. Based on the results of extended X-ray adsorption fine structure (EXAFS) and ^{27}Al nuclear magnetic resonance (^{27}Al -NMR), the partial structure of this new phase was proposed. That is, the SeO_4^{2-} gradually reduced to SeO_3^{2-} under high-temperature calcination and the coordination environment of Se oxoanions also changed from outer-sphere to inner-sphere when the SeO_4^{2-} was reduced to SeO_3^{2-} . This phenomenon is caused by the dehydroxylation, providing electron donor sites on the ettringite. Furthermore, calcination of SeO_4^{2-} bearing ettringite at 800 °C much improved the stability of selenium. This is due to inner-sphere complexation, which is more resistant to remobilization than outer-sphere complexes.

Development of novel and efficient method to stabilize spent absorbents that contain highly toxic ions is urgently needed. In the **Chapter 7**, the use of industrial byproducts as raw materials to produce ceramics to treat toxic waste was investigated. SeO_4^{2-} -doped ettringite was mixed with granulated blast furnace slag (GBFS) and silica fume (SF) and then calcined at various temperatures to produce glass-ceramics. Above 800 °C, the amorphous mixture was converted to glass-ceramics, which were subjected to the toxicity characteristic leaching procedure (TCLP) test. The synthesized ceramics exhibited that lower than 0.1 mg/L of selenate was leached out, and no selenium was evaporated during calcination. In addition, the ceramic materials exhibited excellent chemical stability at pH 2~12. These results showed that industrial byproducts can be successfully applied to produce ceramics for immobilization and storage of hazardous wastes.

Finally, in **Chapter 8**, the main conclusions of this work were summarized.