

First-Principles Investigations into Iodide and Iodate Incorporation Mechanism into Ettringite

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Low-level radioactive wastes are generally stabilized for long-term storage in cementitious materials, where minerals can incorporate radionuclides into their crystal structure. Specifically, as a typical cementitious materials, ettringite is known to stabilize anionic species, which is especially appealing for nuclear waste streams with high levels radioactive iodine isotopes (¹²⁹I and ¹³¹I) that persist as iodide (I⁻) and iodate (IO₃⁻) species in the cementitious nuclear waste repository. In this study, ion chromatography (IC) results suggest that I⁻ incorporation into ettringite is minimal, whereas IO₃⁻ exhibits a high affinity for substitution into ettringite via anion exchange with SO₄²⁻ that results in some distortion to the ettringite crystal lattice. These conclusions are supported by iodine L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra combined with first-principles calculations using periodic density functional theory (DFT). Combination of spectroscopic and computational approach suggests that IO₃⁻ in ettringite is stabilized by both hydrogen bonding and electrostatic forces and that the free energy for substituting IO₃⁻ for SO₄²⁻ is energetically favorable. In contrast, an unfavorable energy barrier was observed for I⁻ substitution for SO₄²⁻ in ettringite. Moreover, the calculated bonding charge density of I⁻ and IO₃⁻ doped ettringite revealed that the IO₃⁻ ions exhibit strong interaction with the structure water molecules in ettringite. However, I⁻ could not interact with structural water molecules. This gives the insights to explain the mechanisms of I⁻ and IO₃⁻ immobilized by ettringite.