

Impact of Ettringite Kinetics and Mineralogy on Tc-99 and I-129 Immobilization in Cementitious Waste Forms

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Cementitious waste forms (CWFs) are the currently planned baseline immobilization approach for liquid and solid secondary waste streams to be generated from vitrification activities at the Hanford Site in Washington State, USA. As well, CWFs are possible candidates to provide a supplemental immobilization pathway for low-activity waste. Within these waste streams, the primary radionuclides of concern are technetium-99 (Tc) and iodine-129 (I) as both are highly mobile as anions, pertechnetate (TcO_4^-), iodide (I^-), and iodate (IO_3^-). Tc retention within CWFs may be improved through reduction to low soluble Tc(IV) species, whereas I retention may be improved through precipitation as low solubility compounds. Yet, as CWFs age and reducing capacity diminishes these Tc and I retention mechanisms may be lost. To this end, alternative mechanisms for improving Tc and I retention are under investigation to assist in CWF long-term performance. Recent work suggests that ettringite [$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$], a common mineral formed in CWFs, may improve Tc retention in CWFs fabricated from high-sulfate waste streams by orders of magnitude. This improvement in Tc retention is hypothesized to be due to anion substitution at the SO_4^{2-} site in ettringite, a mechanism already proven in the literature for IO_3^- . The impact of ettringite formation kinetics on this anionic substitution process is currently unknown, yet hypothesized to be limited with rapid formation. Therefore, this research evaluated Tc and I incorporation during aqueous precipitation of ettringite as a function of ettringite growth rate. Tc and I competition for ettringite incorporation when co-mingled at varying concentrations (10 – 100 ppm TcO_4^- and/or IO_3^-) was also considered. Incorporation of Tc and I into the precipitated ettringite was determined using solution analyses and contaminant incorporation mechanisms were determined from X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) analyses. The results from this work will be discussed in regard to (i) their implications on radionuclide release from CWFs and (ii) how CWF technology development efforts at the Hanford Site may improve current CWF formulations in order to take advantage of the benefits of ettringite growth.