Understanding Tc-99 Immobilization Pathways by Ettringite Formation in Cementitious Waste Forms

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Ensuring immobilization of technetium-99 (Tc) at the Hanford site in Washington State, USA, is a persistent challenge that can be assisted by using cementitious waste form (CWF) treatment technologies. Due to the complexity of the wastes stored and the waste streams to be produced during treatment processes at Hanford, laboratory testing campaigns have explored a variety of CWF formulations for treating a dynamic compositional range of Tc-containing low activity waste (LAW) and secondary waste streams. In one such campaign, studying treatment of a high-sulfate secondary liquid waste stream, formulations with elevated calcium successfully sequestered the sulfate through early ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}$•$26(H_2O)$] formation in the CWF. In these CWF specimens, Tc release (measured as effective diffusivity) decreased by two orders of magnitude relative to previous testing campaigns. This observation suggests that Tc retention within CWFs can be improved by sorption or incorporation of Tc into the ettringite mineral structure. However a molecular level understanding of the mechanism(s) that drive this Tc immobilization is required. This mechanism is expected to differ according to the speciation of Tc in the waste stream. For example, Tc is expected to persist as $Tc(VII)O_4^-$ and $Tc(IV)O_2$ under oxidizing and reducing environments, respectively. To this end, Tc(VII) and Tc(IV) behavior during ettringite formation was simulated using batch precipitation experiments. Mechanistic information was obtained using X-ray diffraction, digital autoradiography, and X-ray absorption spectroscopy. Simularities drawn between characterization of batch experiment samples and simulated CWF specimens were then used to identify how the ettringite immobilization mechanism may change as the CWF ages. The impacts of this mechanistic information towards developing improved CWF technologies will also be discussed.