Understanding Tc-99 Retention in Ettringite for Improving Cementitious Waste Forms

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Immobilizing technetium-99 (Tc) at nuclear weapons waste storage sites, including the Hanford site in Washington State, USA, is a persistent challenge that can be mitigated using cementitious waste form (CWF) treatment technologies. Due to the complexity of the wastes stored at Hanford, laboratory testing campaigns have explored a variety of CWF formulations for treating a dynamic compositional range of Tc-containing low activity waste streams. In one such campaign to study treatment of high-sulfate low activity waste streams, formulations with elevated calcium successfully sequestered the sulfate through ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}•26(H_2O)$] formation in the CWF, during the early stages of curing. In these CWF specimens, Tc effective diffusivity decreased by two orders of magnitude relative to previous testing campaigns that used standard formulations with lower ettringite formation (e.g. Cast Stone).[1] This observation suggests that the improved Tc retention may result from sorption or incorporation of Tc into the crystal structure of ettringite. [1,2] By understanding the mechanism(s) that drive Tc immobilization at the molecular level, improved CWF technologies can be developed to optimize Tc retention.

The possible mechanism for Tc immobilization by ettringite 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, batch precipitation experiments were used to simultaneously precipitate ettringite and observe Tc(VII) or Tc(IV) behavior while ettringite precipitates. Mechanistic information was obtained using X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXFAS) spectroscopy, specifically to determine the final speciation and local coordination environment of Tc after precipitation with ettringite. In this presentation Tc K-edge (21044 eV) XANES and EXAFS results will be discussed and used to explore how controlled mineral growth processes may be manipulated for tailoring CWFs for the immobilization of nuclear wastes.

[1] S.A. Saslow, W. Um, G.L. Smith, D.J. Swanberg, R. Sahajpal. “The Effect of Ettringite on Cementitious Waste Form Development for Low-Activity Waste.” Paper 17170 in Proceedings from Waste Management Symposia 2017. Phoenix, Arizona, March 5 – 9, 2017.

[2] S.A. Saslow, W. Um, R.L. Russell, G. Wang, R.M. Asmussen, R. Sahajpal. “Updated Liquid Secondary Waste Grout Formulation and Preliminary Waste Form Qualification.” PNNL-26443. Pacific Northwest National Laboratory, Richland, Washington (2017).

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