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Characterization of Sorbed Plutonium on Monosodium Titanate

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Introduction: The current proposed design for the Salt Processing Facility at the Savannah River Site include use of monosodium titanate (MST) to remove radiostrontium and selected actinides (Pu, Np and U) from the High Level Waste (HLW) solutions. Little is known about the structure of MST but it most likely contains Ti^{4+} octahedra as opposed to tetrahedral Ti^{4+}. Moreover, it is not known why MST has a strong affinity for actinides such as Pu in alkaline (pH 14) HLW simulant solutions that are rich in Na^{+} ion.

Methods and Materials: To study the chemistry of sorbed Pu on MST in HLW salt simulant solutions we used extended X-ray absorption fine structure spectroscopy (EXAFS), X-ray absorption near-edge structure (XANES) spectroscopy and molecular modeling techniques. Plutonium–loaded MST solids were prepared in HLW salt simulant solutions to have Pu loadings ranging between 553 to ~10,000 mg Pu kg^{-1} MST. The Pu was added to the HLW simulant solutions from acidic stock solutions of Pu(IV) and of Pu(VI). We cannot be certain that the oxidation states of the Pu that we added to the HLW salt solutions and MST remained in their initial forms. The dissolved Pu concentrations in the HLW simulants were too low to unequivocally characterize for oxidation state distributions with analytical techniques. Data collection on Pu-loaded MST was conducted at the L_3 absorption edge of Pu using a 5-grid Lytle fluorescence detector.

Results: The analyses indicate that the sorbed Pu added to the HLW simulant as Pu(IV), is present as Pu species with multiple first shell Pu-O interactions. Higher shell Pu was observed but no higher shell Ti. The Pu-XANES studies indicate these sorbed Pu species had an average oxidation state of Pu(IV). In contrast our first studies, EXAFS analyses for sorbed Pu added initially to the HLW simulant as Pu(VI) indicate this Pu form exists as monomeric Pu species that contain a mixture of oxidized [Pu(V, VI)] and reduced [Pu(III, IV)] species. Higher shell Ti was observed. We conclude that Pu sorbs as monomeric species via an inner sphere adsorption when added originally as Pu(VI) whereas Pu(IV) sorbs as polymeric species that are likely to have a low affinity for surfaces due to their high mass to charge ratios. WSRC-MS-2001-00724.