

Project Title: Characterization of Actinides in Simulated Alkaline Tank Waste Sludges and Leachates

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Research Objective:

During sludge washing procedures associated with tank waste remediation, actinide ions are expected to remain with the insoluble metal oxide/hydroxide residue as the sludges are scrubbed to remove Cr, P, Al, S, and thus to be transmitted conveniently to the vitrification plant. Unfortunately, in laboratory tests with actual sludge samples alkaline sludge treatment has proven less efficacious for Al and Cr removal than was hoped. To improve removal of Al and Cr, more aggressive treatments of sludges are anticipated, including contact with oxidants targeting Cr(III). In addition, our prior research on the alkaline scrubbing of sludge simulants indicated higher than expected “solubilization” of Np and U into concentrated alkali, and some tendency for Am to be mobilized in contact with oxidants. In this project, we are investigating the fundamental chemistry of actinides in sludge simulants under representative oxidative leaching conditions. We are also examining acidic leaching with concurrent secondary separations to enhance Al removal. Our objective is to provide adequate insight into actinide behavior under these conditions to enable prudent decision making as tank waste treatment protocols develop. We expect to identify those components of sludges that are likely to be problematic in the application of oxidative leaching protocols.

Research Progress and Implications:

In our prior investigations, we prepared sludge simulants representative of those that were generated during plutonium production at the Hanford site, specifically representative sludges from BiPO₄, Redox and PUREX processes. Hanford simulants are featured in this program because they are the most diverse of all such materials represented in the DOE weapons complex. These sludges were characterized by a variety of microscopic analysis and element

characterization techniques prior to radionuclide uptake/dissolution tests. At approximately 9 months into the current project, and following upon the success of our initial investigations of actinide behavior in alkali in a prior EMSP project, we have several research activities proceeding in parallel. The several avenues for research include: 1) Investigations of the thermodynamics of formation of hexavalent plutonium mixed complexes with hydroxide and carbonate ions; 2) Oxidative leaching of Np, Pu, and Am from synthetic sludge simulants representing those expected from the BiPO₄, Redox, and PUREX processes; 3) Investigations of the speciation of U(VI) in solutions of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), a complexant that proved particularly efficient in the dissolution of matrix elements (including Al) from sludge simulants. We are able to effectively conduct these parallel studies through the independent work of several postdoctoral research assistants and a visiting scientist and using the complementary facilities at our two institutions. In these three continuing research thrusts, we have learned the following:

1) A combination of near IR spectrophotometric titrations and ¹³C NMR spectroscopy in mixed hydroxycarbonate solutions of Pu(VI) clearly indicated the presence of previously unreported soluble mixed hydroxycarbonate species. We continue this work in an effort to identify the species present and to define thermodynamic parameters for their formation. It appears that (PuO₂(OH)₃CO₃)³⁻ or (PuO₂(OH)₂CO₃)²⁻ may be important solution phase species in addition to the previously known PuO₂(CO₃)₃⁴⁻ and PuO₂(OH)₄²⁻ in solutions of moderate alkalinity (pH 12-14) and 0.06 to 1.5 M total carbonate. These conditions are characteristic of solutions that could be encountered in tank waste supernatants during alkaline scrubbing of sludges. The existence of these new species indicates some probability that higher than expected concentrations of Pu(VI) (and by analogy U(VI) and Np(VI)) might be produced during oxidizing scrubbing of sludges. The eventual determination of thermodynamic parameters will allow these species to be incorporated into computational models of actinide speciation during sludge washing.

2) Oxidative sludge leaching has confirmed the previous observation that a measurable percentage of Am can be mobilized from the sludge simulants under the influence of alkaline oxidants. Other experiments are underway examining the potential solubilization of Pu from sludge samples under the influence of alkaline permanganate. These experiments are being conducted with Pu initially introduced into the sludge phase in both oxidized and reduced forms, in four sludge simulants, and as a function of permanganate concentration (10⁻⁷ to 0.1 M). The latter feature is incorporated into this investigation to gain insight into the potential importance of the Mn reduction product MnO₂ as an actinide sorbent.

3) As noted above, diphosphonic acids might prove particularly useful for Al removal from sludges, hence the speciation of actinides in contact with diphosphonic acids could become important should a complexant like HEDPA be employed for Al removal. Work done previously at ANL has established that gem-diphosphonic acids are quite capable of maintaining moderate concentrations of U(VI) in solution over a wide range of pH (2 to at least 12 and probably higher). Mononuclear UO₂(DPA)₂(H,OH)_n species are believed to dominate speciation in acidic and basic solutions while in the pH 5-11 range polynuclear species of indeterminate stoichiometry ranging down to 1:1 (UO₂:DPA) appear to be most important. These intermediate species clearly must involve polynuclear species with the metal ions bridged either by hydroxide ions or by diphosphonates. We have collected EXAFS spectra of U(VI) in HEDPA as a function of pH to assess which species is more important. Preliminary analysis of the data indicates no significant variation in the immediate coordination environment of the UO₂²⁺ cation in this system. At present, we can therefore not determine the nature of the bridge, though it appears

that a hydroxide bridge is becoming less probable.

Planned Activities:

We expect that the oxidative leaching studies of sludge simulants, both those spiked with actinides (relying on radioanalytical techniques) and those without (subject to conventional analysis to assess Cr removal) will be concluded within the next three months. Most of our subsequent effort will be expended in examining the fundamental chemistry of oxidized actinide ions in strongly complexing media under conditions of alkalinity that are representative of conditions relevant to projected sludge washing scenarios. The existence of mixed complexes (involving more than one ligand, for example, carbonate, oxalate, edta, hydroxide, HEDPA) will provide a particular focus for these studies, as thermodynamic models must take such ill-defined species into account if they are to be of any predictive value during sludge washing. Very little information is available in the existing literature on the characteristics of such complexes. In the third year of this program, we will invest additional effort in developing viable acidic leaching protocols that could enhance removal of Al (which is not redox active and so only leached in oxidative removal as a coincidental effect of matrix disruption during Cr oxidation). Partial dissolution of actinides could also occur during this process, hence processes (most likely based on ion exchange or solvent extraction) for removal of actinides from acidic aluminum nitrate solutions will be investigated. The principal analytical techniques to be employed in most of these investigations include conventional UV-visible-NIR spectrophotometry, NMR spectroscopy, radiochemistry, electrochemistry, and (where relevant) EXAFS.

Information Access:

The new information being developed in this project will be presented at the Boston ACS meeting in August. Experiments on oxidative leaching of sludge simulants are approaching maturity and will be summarized before the end of the year in a manuscript planned for publication in *Environmental Science and Technology*. Our investigation of Pu(VI) speciation in mixed hydroxide-carbonate media is similarly near completion and is projected for publication in *Radiochimica Acta*. Over the next several months, we anticipate being able to provide highlights of these results to the EMSP program office.