

Project Title: Actinide Species in Alkaline Media

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Specific DOE problem being addressed in this project:

The behavior of actinide ions during sludge washing procedures associated with tank waste remediation is currently assumed to be predictable based on information from the literature. The operating assumption is that actinides will remain in the insoluble metal oxide/hydroxide sludge as the sludges are scrubbed with concentrated alkali (to remove Cr, P, Al, S) and thus be transmitted conveniently to the vitrification plant. Due to the complexity of actinide chemistry, the diversity of the sludge materials, the reliance on comparatively few experimental studies of actinide mobilization from such sludges, and the relative paucity of fundamental data to support these assumptions, there is substantial likelihood that actinides will be mobilized under enough conditions to create problems during sludge washing and the subsequent waste processing.

Research Objective:

Using a variety of different techniques, this program attempts to provide relevant fundamental data that will reduce the number of surprises (related to actinide behavior) that occur during sludge washing and tank waste processing. This work builds upon the results of earlier fundamental studies of actinide chemistry in concentrated alkali (many conducted in Russia), on the analysis of tank wastes, and on earlier sludge-specific leaching experiments to gain an improved understanding of the relationship between sludge characteristics and actinide dissolution during proposed sludge washing procedures. A successful outcome for this research will be the generation of sufficient supporting information (both fundamental and empirical) that will enable more accurate prediction of the probability of actinide

dissolution during the scrubbing of sludges from PUREX, REDOX, and BiPO₄ processes. We are studying the mobilization of tri-, tetra-, penta-, and hexavalent actinide cations from sludge simulants; trying to identify mineral phases that might control actinide solubility in sludge simulants; learning about associations between actinide cations and non-radioactive sludge components; investigating the solution-phase chemistry of actinide cations in concentrated alkali; and evaluating the contribution of colloid transport to actinide mobility in sludge washes.

Research Progress and Implications:

At approximately the halfway point of this research project, we have completed most of the experiments dealing with profiling sludge washing using sludge simulants that have been spiked with radiotracer concentrations of uranium, neptunium, plutonium, and americium. The sludge simulants are representative of those that were generated during plutonium production at the Hanford site. Hanford simulants are featured because they are the most diverse of all materials represented in the DOE weapons complex. These sludges have been characterized by a variety of microscopic analysis and element characterization techniques prior to radionuclide uptake/dissolution tests. We have found in simulation of sludge washing procedures that both U and Np can exhibit moderate solubility during alkaline scrubs of sludge simulants while Am and Pu tend to be more insoluble. In the Pu experiments with the Redox sludge simulant, there is some evidence of colloidal transport of Pu. More aggressive leaching/dissolution experiments confirm that substantial (though not selective) dissolution of actinides can be accomplished with dilute acid washes or through the use of organophosphorus complexants. Actinide solubilization often accompanies dissolution of Fe, Cr, and Mn oxides from sludges, suggesting association between actinides and these species. Acidic leaching dissolves phosphate from BiPO₄ sludges which is accompanied by higher leach rates for actinides.

To improve the fundamental science foundation for sludge washing operations, we have in parallel been investigating selected aspects of the chemistry of actinides in strongly basic solutions, focusing on identification of the dominant species present in solution, on developing fundamental thermodynamic data to characterize their solution chemistry, and on the effects of common organic complexants on actinide speciation in such media. Cyclic voltammetry indicates that the Np(VI)-Np(VII) couple is quasi-reversible in LiOH solutions (chosen as a standard medium to reduce problems with actinide precipitation in NaOH solutions), implying substantial structural similarity in the species present. The Np(V)-Np(VI) couple is reversible at [LiOH] ≥ 2 M but irreversible below 1.0 M. We interpret this to indicate that NpO₂(OH)₄³⁻, NpO₂(OH)₄²⁻, and NpO₄(OH)₂³⁻ are the dominant species in strong base. At base concentrations less than 1.0 M LiOH, the Np(V)-Np(VI) couples are irreversible, implying a substantial difference

in the speciation of the ions. In oxalate solutions, the Np(V)-Np(VI) couple is reversible in 1.0 M LiOH while in edta solution, no reversible couples are indicated. Spectrophotometric analysis supports the general conclusions derived from the electrochemistry.

EXAFS investigations of uranyl speciation in the sludge simulants indicate the same pattern in all sludges. In the absence of standard samples to be run as reference materials, we interpret this result to indicate no association between UO_2^{2+} and PO_4^{3-} in the $BiPO_4$ sludge. It is likely that oxides/hydroxides dominate these species. However, it is noted that in these sludge simulants the uranium was deposited/sorbed onto the sludge after the latter had been prepared. More EXAFS investigations will be conducted with the $BiPO_4$ sludge simulants containing uranium that is incorporated into the sludge during the sludge preparation. This additional information will help to clarify whether there is association between UO_2^{2+} and PO_4^{3-} in the $BiPO_4$ sludge. Filtration studies on uranyl leachates from sludge samples indicate up to 10% of the solubilized U in the sludge washing experiments are present on colloidal suspensions which appear to settle out from the solution very slowly (5-7 days). Oxidative scrubbing of sludges (with $K_2S_2O_8$), as might be employed to improve Cr removal from actual sludges, mobilized 10-20% of Am spiked into the sludge. This result could indicate oxidation of Am. Conditions sufficiently oxidizing to take Am to the pentavalent oxidation state would also maintain both Pu and Np as the more soluble oxidized species AnO_2^{+2} .

Our most unexpected result to date has been the relatively high concentrations of uranium mobilized during sludge washing. To the extent actinide cations behave similarly in a given oxidation state, this result could be of great significance for Pu and Np dissolution under oxidizing conditions.

Planned Activities:

Though we have considered conducting sludge leaching studies with actual samples, the cost of such samples (including transportation costs) and of operating remote hot cell facilities to handle such samples cannot be absorbed within the budgetary constraints of this project. Such experiments would be a useful complement to the already completed washing of sludge simulants, but would be most useful only if alternatives to alkaline sludge wash procedures (i.e., sludge dissolution and processing) were still being considered. We plan to focus during the remainder of this research program principally on fundamental aspects of actinide chemistry in alkaline solutions relevant to sludge washing. Experiments planned or in progress will investigate the chemistry of Np, Pu, and U in alkaline solutions containing varying concentrations of water-soluble chelating agents of importance in tank waste treatment, e.g., oxalate, glycolate, edta, nta at varying

concentrations of base and carbonate. The possible existence of mixed-ligand complexes will be investigated. The principal analytical techniques to be employed include conventional UV-visible-NIR spectrophotometry, NMR spectroscopy, radiochemistry, electrochemistry, and (where relevant) EXAFS.

Information Access:

Oral presentations have been made at the 11th Symposium for Separation Science and Technology for Energy Applications and the EMSP Atlanta workshop. A third oral presentation will be made in August at the 24th Actinide Separations Conference. Poster presentations have been made at the New Orleans, two at the San Francisco American Chemical Society meetings, one at the Materials Research Society meeting in Boston in the fall of 1999, at the EMSP Atlanta Workshop. One additional poster presentation is planned for the ACS meeting in Washington D.C. in August. Our poster at the MRS meeting in Boston, won a poster award, marking it in the top 1% of all posters presented. Two research papers are in press. Two additional papers are in preparation. Several more will follow from the next stage of this project.