

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

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***Research Objective:***

Treatment of underground tanks at Hanford with concentrated alkali to improve removal of waste-limiting components of sludges has proven less efficacious for Al and Cr removal than had been hoped. Hence, more aggressive treatments of sludges, including contact with oxidants targeting Cr(III), have been tested in a limited number of samples and found to enhance Cr removal. Unfortunately, treatments of sludge samples with oxidative alkaline leachates produce conditions under which normally insoluble actinide ions (e.g.,  $\text{Am}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Np}^{4+}$ ) can no longer be reliably assumed to remain in the sludge phase. Few experimental or meaningful theoretical studies of actinide chemistry in strongly alkaline, strongly oxidizing solutions have been completed. Extrapolation of acid phase thermodynamic data to these radically different conditions provides little reliable guidance for predicting actinide speciation in highly salted alkaline solutions. In this project, we are investigating the fundamental chemistry of actinides in sludge simulants and supernatants under representative oxidative leaching conditions. We are also examining the potential impact of 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  $\text{BiPO}_4$ , Redox and PUREX processes, using accepted model formulations. 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 our present stage of one year and 8 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 continuing in parallel.

- We have completed our investigation of the thermodynamics of formation of hexavalent plutonium mixed complexes with hydroxide and carbonate ions, identifying the previously unknown mononuclear species  $\text{PuO}_2(\text{OH})_2\text{CO}_3^{2-}$  and  $\text{PuO}_2(\text{OH})_3\text{CO}_3^{3-}$ . We have also determined equilibrium constants for the formation of these species that will allow us to assess their relative importance under sludge scrubbing conditions. These species are representative of those that might be expected to dominate the solution-phase speciation of Pu(VI) in that range of conditions between carbonate-rich solutions ( $\text{PuO}_2(\text{CO}_3)_3^{4-}$ ) and concentrated (above 1 M) alkali ( $\text{PuO}_2(\text{OH})_4^{2-}$ ). As such, they could act to increase solubility of Pu(VI) above that predicted using currently available thermodynamic data. Knowing of the existence of these mixed complexes will enable more accurate predictions to be made of Pu solubility in alkali. With the new thermodynamic data in hand, we plan to perform calculations of the thermodynamics of Pu speciation to determine under what conditions these species might interfere with plutonium solubility controlled by  $\text{PuO}_2(\text{OH})_2$ .
- Studies of the oxidative leaching of Pu and Am from the synthetic sludge simulants verify that Cr(III) is oxidized to  $\text{CrO}_4^{2-}$  and thus solubilized, but also that both Pu and Am can be oxidized by alkaline permanganate. The  $\text{MnO}_2$  produced as permanganate is consumed assists the natural actinide sorption tendencies of the sludge simulants, but the presence of competing reductants (for example, organic complexants) can complicate speciation. We find that the permanganate-manganate equilibrium lies in the manganate stability field due to kinetically facile  $\text{OH}^-$  oxidation by  $\text{MnO}_4^-$ , hence one equivalent of the potential oxidizing capacity of permanganate is lost to unproductive reactions if the solutions are allowed to sit for 24 hour prior to use. The manganate oxidant exhibits oxidative power nearly identical to permanganate, so oxidation still proceeds apace. A kinetic barrier prevents further oxidation of  $\text{OH}^-$  by free manganate ion. We have observed that manganate/permanganate reacts comparatively quickly with gluconate, glycolate and edta but does not oxidize either oxalate or citrate in concentrated alkali (though it is well-known that such oxidation occurs in acidic solutions). These experiments have been conducted with Pu initially introduced into the sludge phase in either oxidized or reduced forms, in four sludge simulants, and as a function of permanganate concentration ( $10^{-7}$  to 0.1 M). These experiments were run using  $^{238}\text{Pu}$  at  $10^{-9}$  M total plutonium and quantified using radiometric detection. Similar patterns of plutonium “solubilization” were observed independent of the initial oxidation state of the Pu. Our studies indicate that oxidizable components of sludge could profoundly impact both Cr(III) oxidation and Pu solubilization.

Our stage one (first funding cycle) investigation indicated improved Al leaching from sludge simulants in acidic solutions and in those containing diphosphonate chelating agents. Acid/complexant leaching of sludges could improve Al removal efficiency, but these same conditions are known to impact actinide speciation as well. This program also has the objective of characterizing the chemistry of actinides in such solutions. We are therefore conducting 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 Al from sludge simulants. 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). The previous work indicated that mononuclear  $\text{UO}_2(\text{DPA})_2(\text{H},\text{OH})_n$  species dominate speciation in acidic and basic solutions while in the pH 5-11 range polynuclear species of indeterminate stoichiometry ranging down to 1:1 ( $\text{UO}_2$ :DPA) appear to be most important. Our recent work on the thermodynamics of this system reproduces certain features of this chemistry that was previously reported, while yielding a different interpretation of other features. Recent potentiometric titration and calorimetry results have been interpreted to indicate the predominance of 1:2  $\text{UO}_2(\text{VI})$ :HEDPA complexes ( $\text{ML}_2\text{H}_x$ ) in the intermediate pH regime rather than the polynuclear species postulated previously. Our earlier EXAFS investigations of U(VI)-HEDPA solutions are consistent with the interpretation that the inner coordination sphere of  $\text{UO}_2^{2+}$  is not significantly altered across the pH 2-11 range, indicating that hydroxide-bridged polynuclear uranyl hydroxides are probably absent in these solutions.

### ***Planned Activities:***

Planned oxidative leaching studies of sludge simulants have been completed. Work continues on describing the thermodynamics and speciation of actinide complexes with HEDPA in neutral and alkaline solutions. The primary emphasis of the next stage of our studies will be on characterization of actinide-diphosphonate complexes in neutral and alkaline solutions and on the performance of the proposed  $\text{Al}(\text{NO}_3)_3$  dissolution with separations cleanup to remove actinides. We will examine as well the question of whether alkaline oxidation conditions impact substantially the stability of HEDPA. We have also proposed to investigate conventional separations procedures (ion exchange, solvent extraction) as a means to remove actinides from acidic  $\text{Al}(\text{NO}_3)_3$  solutions using (for example) CMPO and/or ion exchange resins. We also are considering experiments to follow on the Pu(VI)-hydroxycarbonate speciation study searching specifically for the presence of mixed hydroxy-citrate or hydroxy-oxalate complexes (each species known to form strong complexes with hexavalent actinides and, based on our observations, resistant to alkaline permanganate oxidation), though these studies are considered of secondary importance to the  $\text{Al}(\text{NO}_3)_3$  actinide decontamination studies at present. The principal analytical techniques to be employed in most of these investigations include conventional UV-visible-NIR spectrophotometry, NMR spectroscopy, radiochemistry, electrochemistry, calorimetry, and (where relevant) EXAFS.

### ***Information Access:***

To date, presentations have been made on results obtained in this program at several American Chemical Society national meetings, at consecutive Actinide Separations Conferences, and at the EMSP PI's workshop in May, 2003. We will also be participating in the EMSP symposium planned for the fall 2003 American Chemical Society meeting in New York City. Several manuscripts are in preparation with planned publication in *Environmental Science and Technology*, *Separation Science and Technology* and *Radiochimica Acta*. We are working on programmatic highlights to be submitted to the program office as well.