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ACTINIDES IN HANFORD TANK WASTE SIMULANTS: CHEMISTRY OF SELECTED SPECIES IN OXIDIZING ALKALINE SOLUTIONS

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To enhance removal of selected troublesome nonradioactive matrix elements (P, Cr, Al, S) from the sludges in radioactive waste tanks at the Hanford site, various chemical washing procedures have been evaluated. It is intended that leaching should leave the actinides in the residual sludge phase for direct vitrification. To remove Cr from sludges, oxidative treatment with strongly alkaline solutions has emerged as the best approach to accomplishing this feat. However, because the most important actinide ions in the sludge can exist in multiple oxidation states, it is conceivable that changes in actinide oxidation state speciation could interfere with hopes and plans for actinide insolubility. In this presentation, we discuss both the impact of oxidative alkaline leachants on actinide oxidation state speciation and the chemistry of oxidized actinide species in the solution phase. Actinide oxidation does occur during leaching, but solubility behavior is complex. Mixed ligand complexes may dominate solution phase speciation of actinides under some circumstances.

This work has proceeded with several parallel activities being conducted in tandem. We have examined the leaching behavior of U, Np, Pu and Am from synthesized simulants of sludges representative of those generated during plutonium production at Hanford.

Over that 40+ year period (1943 to 1986), the Bismuth Phosphate, Redox and PUREX processes all operated at Hanford for plutonium recovery from dissolved spent fuel. Each of these processes generated distinct effluents, which were made alkaline and disposed to the tanks. Over the years, these samples were mixed from tank to tank, effluents were evaporated to remove excess water and were subject to thermal and radiolytic degradation. As a result, the sludges in the tanks today represent an extremely diverse mixture of materials. To gain a predictive capability for actinide performance during sludge washing, we approached this study with the understanding that we would gain far more useful insights by investigating the simulants than could be gained from investigating leaching from actual tank sludge samples (though studies with actual samples are invaluable for validation and process development purposes).

Our simulant leaching studies have allowed us to conclude that there is real potential for actinide solubilization during sludge washing. Leaching of Pu-spiked sludge samples with alkaline permanganate have established that MnO_4^-/MnO_4^{2-} (the conversion of permanganate to manganate is spontaneous and complete within 24 hours in 3.0 NaOH) successfully leaches Cr from the sludge samples. The order of Cr content of the sludge simulants is Redox>$BiPO_4$>>PUREX. Oxidation of Cr(III) to Cr(VI) is accompanied by the generation of Mn(IV), which in alkaline solutions immediately precipitates as MnO_2. The latter is well known as an effective sorbent for Pu. We observed that while the total oxidizing capacity remained below the total content of Cr in the samples (*i.e.*, excess Mn(VII)/Mn(VI) is not present in the solution phase), Pu remained in the solid phase (whether it stays in the sludge or is sorbed onto MnO_2 was not determined). When excess Mn(VII/VI) is present, leached Pu concentration increases. We observed as well that organic complexants reacted with the excess Mn(VII/VI) to further complicate Pu solution/solid speciation patterns. Not all organic materials were susceptible to oxidation by alkaline permanganate. Oxalate and citrate in particular proved resistant.

Studies of the leaching potential of Am from the same sludge simulants by alkaline persulfate and permanganate likewise produced unexpected increases of Am concentrations in the leachates. The rates of leaching varied with the type of sludge, with contact time, temperature and concentration of oxidant. Mn(VII/VI) was found to leach 10-50% of the radiotracer Am present in the sludge simulants. Increasing concentration of base (1.0-3.0-5.0 M) in the leachate led to increased leaching. Temperature had a comparatively lesser effect. Kinetics of the persulfate system are slower, but similar amounts of Am are leached as are seen in the Mn(VII/VI) system. It appears likely that some conversion of Am to oxidized species (most rationally, Am(V)) is occurring. Whether this solubilization is important during alkaline leaching will be a function of the time that lapses between leaching and vitrification (Am(V) is unstable even in strong alkali, but the kinetics of reduction is comparatively slow in the absence of reducible substrates).

To enhance leaching of Al(III) from the sludge simulants, our earlier studies established increased efficiency for leaching of the sludge samples with 1) comparatively dilute HNO_3 (up to 1 M) and 2) the addition of acidic diphosphonate complexants. Those

studies established that the nitric acid had only a minor impact on actinide solubilizations from sludge (in short contacts at room temperature) but that the complexant had a larger impact, partly due to extensive matrix dissolution. If such a leaching protocol were to be adopted, we would need more complete insight into the chemistry of the actinides in contact with these complexing agents. Studies of these systems have been conducted in acidic solutions, but neutral-alkaline solution speciation studies of actinide-diphosphonates are incomplete. We are therefore engaged in an investigation of the thermodynamic features of uranyl complexation by 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). To date, we have determined that the speciation appears to be dominated by 1:1 and 1:2 complexes between U(VI) and HEDPA. Planned complementary studies will examine the behavior of Al in this system in addition to fundamental investigations of uranyl complexes with other diphosphonate complexants.

Returning to the scenario of solubilization of oxidized actinides in strongly alkaline solutions, thermodynamic modeling is heavily relied upon to predict the behavior of these metal ions under conditions that may not have been explicitly investigated from a phenomenological perspective. However, speciation calculations based on thermodynamic data will not provide accurate predictions if unidentified species are present in the system. In our earlier investigations, we established the existence of previously unreported Np(V) hydroxide and mixed hydroxy-carbonate complexes in strongly alkaline solutions and estimated experimentally reversible oxidation/reduction potentials for Np(V/VI/VII) hydroxides in concentrated hydroxide solutions. We have continued this portion of our investigation with a similar study of Pu(VI) speciation in mixed hydroxy carbonate solutions. Relying principally on spectrophotometry, we have tentatively identified a new Pu(VI) mixed hydroxycarbonate complex that helps to define what species might be created in the transition from the hexagonal bipyramidal plutonyl(VI) tris carbonato somplex ($PuO_2(CO_3)_3^{4-}$) that dominates Pu(VI) speciation over a wide range of pH and carbonate concentrations and the octahedral tetrahydroxide ($PuO_2(OH)_4^{2-}$) that predominates in strongly basic solutions. Both carbonate and hydroxide species are present during alkaline leaching of sludges and so it is quite reasonable to expect that species of this type could be created during sludge leaching. Our studies of oxidant interactions with chelating agents in strongly basic solutions have suggested to us that further studies of mixed hydroxy-oxalate or hydroxy citrate complexes (both were resistant to alkaline permanganate oxidation) might also be important species to investigate under these conditions. We are planning prelimary scoping studies to assess this potential in the coming months. This work was supported by the U.S. Department of Energy, Offices of Science and Waste Management, Environmental Management Science Program under Contract DE-AC03-76SF0098 at Lawrence Berkeley National Laboratory and Contract W-31-109-ENG-38 at Argonne National Laboratory.