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**CHARACTERIZATION OF ACTINIDES IN
SIMULATED ALKALINE TANK WASTE SLUDGES AND LEACHATES**

EMSP Project ID number 81940

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Project began as collaboration between Argonne National Laboratory and Lawrence Berkeley National Lab, moving to Washington State University with the PI in August 2003.

RESEARCH OBJECTIVES

This project was begun within the EMSP program in FY 1998 with the objective of developing guiding principles for predicting actinide behavior in the concentrated alkali most relevant to alkaline tank waste remediation (as found at both Hanford and Savannah River). During the first stage, sludge simulants were prepared that combine non-radioactive components of the major chemical processes used at Hanford during its 40+ years of plutonium production (PUREX, REDOX and Bismuth Phosphate). Work focused on the Hanford tanks primarily because they contain a substantial fraction of the DOE process wastes needing remediation, but also because their contents represent by far the greatest diversity of components in tank wastes. Due to the identical tank construction materials, the alkaline media for storage, and the impacts of time, temperature and radiation, at least some of the materials in the Hanford tanks are representative of similar materials existing at other actinide production facilities. Exploratory leaching studies established the potential utility of acidic and complexometric leaching of sludges and verified that most actinides remained in the sludge phase after leaching. The fundamental features of actinide chemistry in alkaline solutions were also investigated.

At the second stage of development of this project (after the first renewal), it had become apparent that removal of waste-limiting components of sludge (Al, Cr, S, P) in underground tanks at Hanford by treatment with concentrated alkali had proven less efficacious for Al and Cr removal than had been hoped. More aggressive treatments of sludges, for example, contact with oxidants targeting Cr(III), were tested in a limited number of samples and found to improve leaching efficiency for Cr. Oxidative alkaline leaching can be expected to have at best a secondary influence on the mobilization of Al. Earlier explorations in this project of Al leaching from sludge simulants indicated acidic and complexometric leaching can improve Al dissolution. Unfortunately, treatments of sludge samples with oxidative alkaline, acidic or complexing leachates produce conditions under which normally insoluble actinide ions (e.g., Am^{3+}, Pu^{4+}, Np^{4+}) were more readily mobilized to the solution phase. Few experimental or meaningful theoretical studies of actinide chemistry in strongly alkaline, strongly oxidizing solutions have been completed, so prediction of this behavior based on existing information was not possible. Further, extrapolation of the more abundant acid phase actinide thermodynamic data to these radically different conditions provided limited reliable guidance for predicting actinide speciation in highly salted alkaline solutions.

At the third stage of this project (second renewal), investigations of the fundamental chemistry of actinides and important sludge components in sludge simulants and supernatants under representative oxidative leaching conditions complemented further oxidative leaching studies and explicit strategies for decontaminating leachates containing radioactive isotopes. The potential impact of acidic or complexometric leaching with concurrent secondary separations on Al removal from sludges was also initiated. Finally, a portion of this research was directed at the control of polyvalent anions ($SO_4^=$, $CrO_4^=$, PO_4^{3-}) in waste streams destined for vitrification. The primary objective throughout this investigation was to provide adequate insight into actinide behavior under sludge leaching conditions to enable prudent decision making as tank waste treatment protocols developed.

Accomplishments:

Sludge Leaching Studies stage one

The sludge simulants for wastes from the three plutonium production processes vary substantially in composition. Analysis of the synthesized sludges indicated that the Cycle 3 $BiPO_4$ sludge is about 36% by weight $BiPO_4$. This sample contains about 11% lanthanides (from LaF_3 precipitation) and has the highest concentration of manganese (7%) and Cr (5%) of the three sludge types. The Redox sludge simulant is 24% Al and contains 4% Cr, 5% Fe, and 1% Mn. The PUREX sludge simulant is highest in Fe (24%) but also contains 7% Al and 2% Mn but no Cr. There is a "volatiles" fraction in each sludge stimulant representing principally water in each of these simulants, but also organic materials that are present in actual tank sludges.

Both baseline and exploratory leachings of sludge simulant samples spiked with radiotracer concentrations of U, Np(V), Am(III), Sr(II) and both oxidized and reduced Pu were conducted. The leachants (in most cases applied consecutively to the same spiked sludge samples) included: 0.01 M $NaNO_2$ + 0.01 M NaOH (sluicing liquid from Hanford baseline strategy); 3.0 M NaOH (leachant from Hanford baseline strategy); H_2O; 0.05 M Glycolic Acid + 0.10 M NaOH (weak complexant, dilute base); 0.10 M HNO_3 (dilute acid); 2.0 M HNO_3 (moderate acid); 0.50 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA – strong, acidic complexant). All of these studies were conducted at room temperature and involved equilibration times of less than 24 hours. The first three solutions represent baseline sludge washing solutions. The latter four leachants are experimental solutions designed to teach us how resistant to leaching the sludge components are, and, with the radiotracer experiment, to establish which non-radioactive components tend to be associated with the actinides. In addition to assaying mobilized actinides, the amount of Al, P and Cr dissolved in the leach treatment of the sludge samples were also determined. Some sludge washings were performed using parallel (rather than series) contacts with these solutions. In many cases, near complete dissolution of the sludge sample was achieved with this 7-stage leaching process.

It was observed that some (but not all) of the Cr(VI) is removed from the sludge samples in the 3.0 M NaOH wash. The exploratory washes with more aggressive reagents demonstrated substantial dissolution of Fe from both the PUREX and Redox sludges in 0.1 M HNO_3. The 2.0 M HNO_3 wash solubilizes additional Fe, the lanthanides, and the reduced chromium species, presumed to be Cr_2O_3. The wash with HEDPA leads to dissolution of Mn. Most of these species

were identified spectrophotometrically. Aluminum analysis indicates 66% of the aluminum in the Redox and 21% of PUREX Al dissolves in 0.1 M HNO_3; 6% of Redox, 22% of PUREX Al dissolves in 2.0 M HNO_3; 10% Redox, 32% PUREX Al dissolves in HEDPA. The aluminum sludge washes describe parallel rather than consecutive contacts and thus do not demonstrate the cumulative effect of the leachants. The comparative recalcitrance of Al toward dissolution by these reagents, particularly in the PUREX sludge simulant, was somewhat surprising, but also consistent with reports of poorly-soluble Al in actual sludge samples. These results also indicate an opportunity for enhanced Al leaching with an acidic leaching protocol.

In the parallel experiments with sludges to which actinides have been adsorbed, only very small amounts of Pu (whether introduced to the sludge in the oxidized (Pu(VI)) or reduced (Pu(III/IV)) forms) and Am were observed in the baseline sludge wash supernatants from all of the sludges. In the exploratory washes, americium behaved exactly like the lanthanides, dissolving quantitatively in the 2.0 M HNO_3 leachate from each sludge simulant. Plutonium behavior is more complex. About 30% of either oxidized or reduced Pu dissolved from the Redox sludge simulant in 0.1 M HNO_3 coinciding with the dissolution of about 66% of the aluminum from that sludge. Upon filtration, the Pu was removed from the sample, suggesting a high probability that the 20-30% is adsorbed on alumina colloids in this sample rather than in true solution. A moderate percentage for Pu (oxidized and reduced) was removed in the 2.0 M HNO_3 leachate of the modified $BiPO_4$ sludge. This material was not filterable thus not radiocolloidal, but in true solution. Elemental analysis of this sample strongly suggests that it has a significant percentage of lanthanide phosphate in addition to bismuth phosphate. The apparent relative increase in Pu in solution perhaps reflects the greater solubility of $LnPO_4$ (relative to $BiPO_4$) in 2.0 M nitric acid. Generally less than 10% of the radiotracer Pu was solubilized from Redox and PUREX sludge simulants with only minor differences between Pu initially oxidized and reduced. Colorimetric analysis indicates substantial dissolution of Fe_2O_3 and Cr_2O_3 in these leachates. One possible implication of this result is that $PuO_2(s)$ may well be controlling Pu solubility (though these experiments were conduced using [238]Pu tracer, for which the thermodynamic solubility limits would not necessarily be exceeded). Upon contact with the HEDPA chelating agent, somewhat larger amounts of oxidized Pu than reduced are dissolved. Colorimetric analysis indicates dissolved Mn(III) or Mn(IV) (from MnO_2) in this leachate.

Leaching studies stage 2 – oxidative leaching mobilized Am The considerable disruption of the solid matrix that must occur during this oxidative leaching exposes not only reduced Cr species to solubilization, but can also expose oxidizable actinide ions to the same fate. Oxidative leaching of (sorbed) Pu from each sludge simulant with alkaline permanganate (3.0 M NaOH/ variable permanganate) resulted in significant increases in plutonium content of the leachate, as shown in Figure 1 top. The concentration of Pu in the solution phase increased with the permanganate concentration. Similar concentrations of Pu were found in the leachate independent of the initial oxidation state of the Pu. The parallel increase of Pu and Cr concentrations in the leachate are consistent with the suggestion that matrix disruption exposes actinides to potential mobilization by alkaline oxidants. The amount of Pu released from the sludges was notably lower from the $BiPO_4$ sludge sample than from the Redox or PUREX sludge simulants, perhaps indicating the actinide mobility retardation properties of phosphate solids. The potential of organophosphorus compounds to retard actinide mobility has been previously

investigated. Other investigators have considered the potential utility of hydroxyapatite for such applications.

Because alkaline permanganate is such a potent oxidant, it is expected that it will be consumed in reactions with any oxidizable species that is present in the sludge. The nature of interactions of permanganate with several organic complexants that are known to exist in Hanford waste tanks was also examined. The oxidation of oxalate, citrate, glycolate, gluconate, and edta by permanganate was assessed, contacting solutions containing varying concentrations of each organic complexant with 0.1 M $KMnO_4$ in 3.0 M NaOH. The amount of Mn(VII/VI) consumed was determined colorimetrically. Radiotracer [238]Pu was present in all experiments. It was anticipated based on earlier observations of Np speciation in concentrated base (discussed below) that the predominant Pu species should be soluble $PuO_2(OH)_4^=$

Figure 1. Permanganate effect on chromium (bottom) and plutonium (top) leaching from sludge simulants.

under these conditions (permanganate oxidation should convert any potentially solubility limiting PuO_2 to the more soluble hexavalent oxidation state). Therefore, any Pu removed from
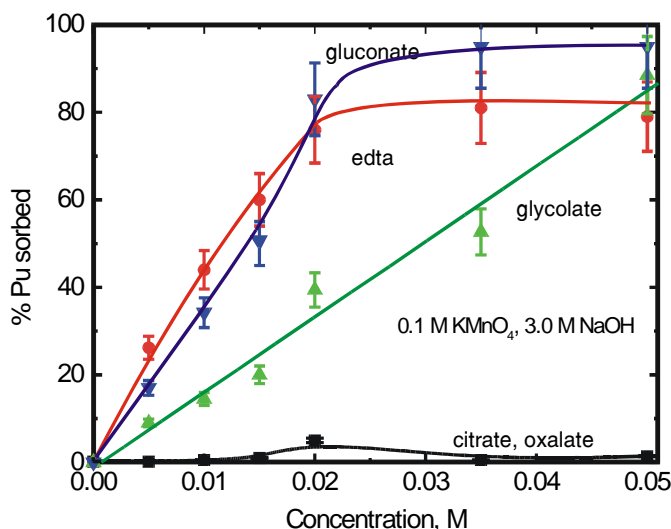

Figure 2. Plutonium sorbed from solution as a function of organic complexant oxidation by permanganate.
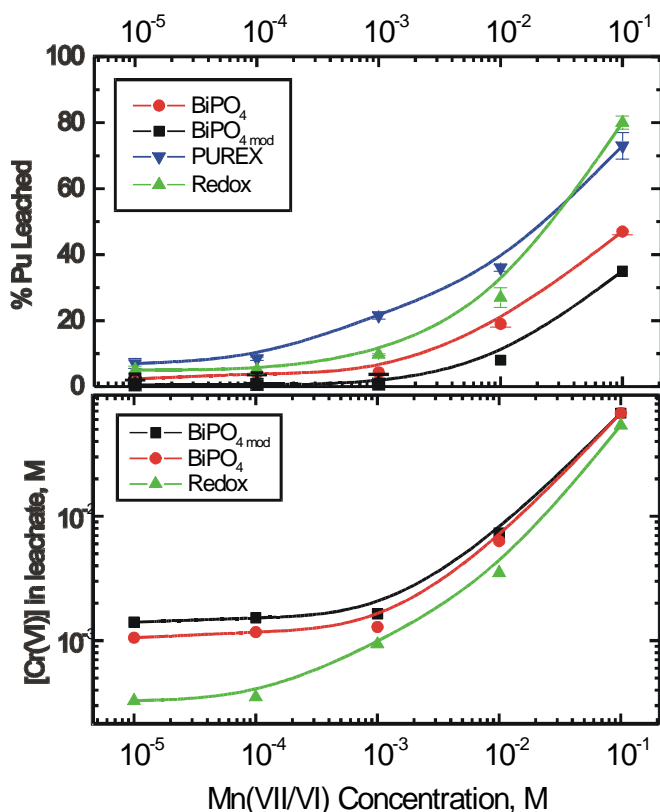
the solution must be sorbed to the MnO_2 byproduct of oxidation. As the data in Figure 2 indicate, glycolate, gluconate and edta were oxidized (and Pu(VI) sorbed onto MnO_2) while oxalate and citrate proved resistant to oxidation (and thus to MnO_2 generation). Assuming that the removal of Pu from the supernatant solution was strictly through the agency of sorption onto MnO_2, it can be seen that the amount of Pu removed from the solution phase correlated in a linear fashion with the amount of byproduct MnO_2, as shown in Figure 3.

This relationship persisted independent of which complexant was used to create the MnO_2 sorbent. The residual organic degradation byproducts had no impact on Pu concentrations in the supernatant solution, that is, where present, sorption onto MnO_2 controlled Pu concentrations in the solution phase. The resistance of citrate and oxalate to oxidation by permanganate is almost certainly related to the absence of a sufficiently reactive center (secondary alcohol or tertiary amine groups are present in glycolate, gluconate, and edta – oxalate and citrate have no similar functional groups). There have been no prior investigations of the oxidation of these organic complexants by alkaline permanganate. The practical implications of these observations for tank waste remediation are twofold, 1) many, but not all, organics present in tank wastes could be oxidized to harmless materials by alkaline permanganate, and 2) that appropriate organic materials could be used to consume excess oxidant during leaching for Cr(III) removal. The concomitant production of MnO_2 as a byproduct could potentially limit the degree to which actinides might be unintentionally mobilized from the sludge. These results also suggest that oxalate and citrate might become important complexants in such media.
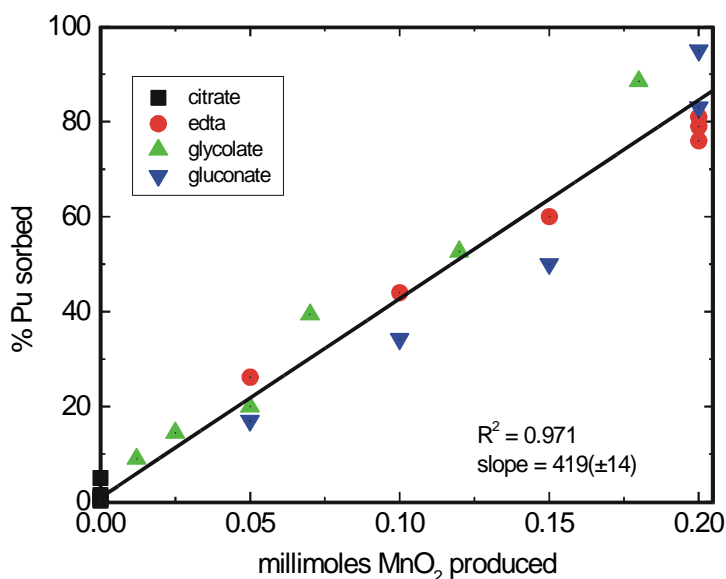

Figure 3. Correlation of Pu sorption from alkaline solutions with MnO_2 produced during complexant oxidation by permanganate.

To further assess the potential for coincidental actinide mobilization during oxidative leaching of tank waste sludges, the leaching of Am-containing sludge samples by alkaline persulfate was also examined. Though all oxidation states of Am above the trivalent are potent oxidants in acidic solutions, initial investigations indicated some potential for enhanced Am dissolution by alkaline persulfate. In a more thorough investigation, it has been observed that up to 60% of the Am sorbed onto the four sludge simulants was released to the solution phase upon treatment of the sludge samples with alkaline persulfate solutions. The maximum percentage of leached Am from each sludge simulant is shown to increase with increasing concentration of NaOH in Figure 4. Kinetic analysis of these data indicated that the rates of Am oxidation/ mobilization increased in the order $BiPO_4$ < Redox < PUREX. Though one would not expect the oxidized Am to remain stable in the supernatant in the long term, it was noted that the maximum concentration was maintained for at least 24 hours in most experiments. It is therefore conceivable that oxidative leaching could promote some removal of Am from actual sludge samples and maintain elevated concentrations long enough to become problematic during oxidative alkaline leaching to remove Cr. Whether a similar result might be obtained for Am leaching with permanganate was not assessed.

Both Np and U are most stable in solution as oxidized species, hence are less likely to be impacted as significantly by oxidizing agents as the typically reduced Am and Pu species. As noted above, oxidized actinides tend to exhibit higher solubility limits. In the baseline sludge washing process, 3.0 M NaOH removes about 25% of the radiotracer [237]Np and 10-15 % of its [233]Pa daughter. The Np appears to be in true solution. The dilute acid leach removed a small amount of the Np from the Redox sludge, but none from any other samples. The 2.0 M HNO$_3$ wash dissolved at least 50%

Figure 4. Maximum Am leached from sludge simulants by 0.1 M persulfate as a function of NaOH concentration.

of all of the Np from all sludge samples. The remaining 10-20% dissolved with the HEDPA wash. Not surprisingly (due to the substantial differences in their chemistries), the [233]Pa daughter dissolved in the opposite pattern, i.e., more in the HEDPA than in the HNO$_3$ leachate.
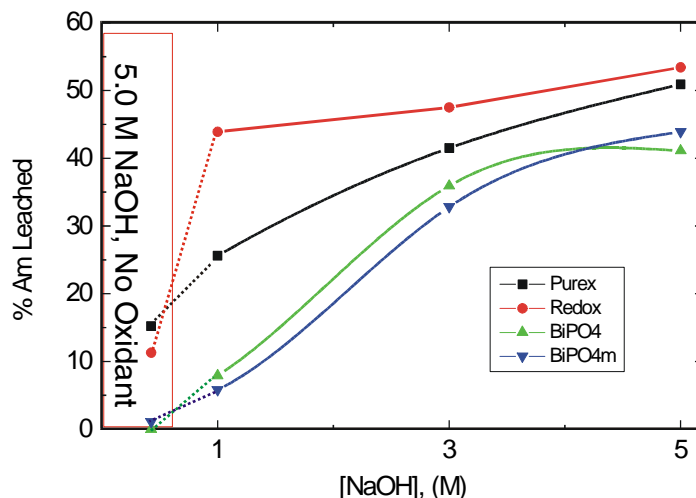
Studies of leaching of U(VI) from sludges were conducted at tracer level using [233]U and a macroscopic concentration ([238]U, 0.5% by weight in the sludge) from a solution of 0.10 M Na$_2$CO$_3$/0.50 M NaOH/1.0 M NaNO$_3$. In addition, the Redox sludge simulant contains about 0.45% (by weight) [238]U that was incorporated into the sludge during the sludge preparation process. Sludge leaching for U samples was done in a parallel (rather than serial) fashion, as the serial washing left little material for the final washings. The leaching efficiencies of U by 0.01 M NaOH/0.01 M NaNO$_2$, H$_2$O, and 0.1 M NaOH/0.05 M glycolic acid were generally low from all four sludges. Less than 1% of U was found in these leaching solutions from BiPO$_4$ sludges. For PUREX and Redox sludges, the percentage of U in these leachates was up to 16% for PUREX and 24% for Redox sludges, which parallels the aluminum dissolution that was observed during these treatments. The U was quantitatively dissolved in the HEDPA and 2.0 M HNO$_3$ leachates, 30-60% dissolved in 0.1 M HNO$_3$. Generally speaking, the leaching efficiencies at tracer and macro levels are quite similar for all the four sludges. However, in the 3 M NaOH leaching from Redox and PUREX sludges 82%-89% of [233]U (tracer only) was found in the leachate while only ~15% of [238]U (macro U experiment) was found in the same leachate (corresponding to ~ 2 10^{-5} M U in 3 M NaOH). This difference suggests that reprecipitation of uranium solubility limiting solids is possible at macroscopic concentrations that is clearly not operable in the radiotracer experiments. EXAFS examination of macro uranium on the sludge samples indicated that the uranyl coordination environment was different in each sludge. Only the spectra for the Redox sludge are similar to that of uranyl hydroxide. This implies that U(VI) is probably incorporated into the two BiPO$_4$ sludges and the PUREX sludge rather than being precipitated as hydrolysis products on the surface. No evidence was found for the coordination of U(VI) with phosphate in the two BiPO$_4$ sludges.

Speciation of Actinide Ions in Alkaline Solutions:

Actinide electrochemistry in alkaline solutions

The results of sludge leaching experiments done earlier in this project made it clear that it is most important to profile the speciation of the hexavalent and pentavalent actinide ions in alkaline solutions. The most stable species representing these oxidation states are U(IV) and Np(V). As permanganate or persulfate are added, these leaching studies indicate that Pu(VI) or even Am(V) can become important solution phase species. The focus of macro-scale actinide speciation efforts was on U(VI), Pu(VI), and Np(V). The Np investigation employed UV-Visible-Near IR spectrophotometry, radiochemistry, and electrochemistry to establish that at base concentrations above 1.0 M the nearly isostructural ions $NpO_2(OH)_4^{3-}$, $NpO_2(OH)_4^{2-}$, and $NpO_4(OH)_2^{3-}$ are the dominant species of Np(V, VI, VII) in the absence of complexing anions. The experimentally determined E^o values for Np(VI/V) and Np(VII/VI) in these media are +0.106V and +0.450V. The electrochemically irreversible reduction of Np(V) to NpO_2 appears to begin in the vicinity of E^o = -0.15 V. These values compare with the respective estimated standard potentials of +0.38, +0.58, and –0.09 V. Results of electrochemical experiments in the presence of carbonate and hydroxide support the observations of Neck and coworkers (*V. Neck, et al., Radiochim. Acta 77, 167 (1997)*) that mixed mononuclear hydroxycarbonates dominate the speciation of Np(V) and Np(VI) when both carbonate and hydroxide are present. Np(VII) does not appear to interact significantly with $CO_3^=$ at concentrations below 0.3 M total carbonate, as evidenced by the electrochemically irreversible cyclic voltammogram for the Np(VI/VII) couple under these conditions. At base concentrations above 6 M (in the presence of 0.3 M carbonate), the hydroxide species noted above again appear to dominate the speciation of Np(V, VI, and VII). It has been demonstrated that Np(VII) oxidizes various organic complexants in 1.0 M base at quite different rates. The corresponding Pu(VII) species requires even higher base concentrations (13 M) for stabilization.

Actinide carbonate complexes To augment the Np speciation work, the chemistry of Pu(VI) in mixed hydroxycarbonate solutions was investigated. It is well known that the hexagonalbipyramidal triscarbonato complex $(PuO_2(CO_3)_3^{4-})$ dominates the speciation of plutonium(VI) from about pH 6 to 12 when carbonate/bicarbonate is present and that the centrosymmetric square bipyramidal tetrahydroxide $(PuO_2(OH)_4^{2-})$ dominates Pu(VI) speciation in concentrated base solutions. An extended series of spectrophotometric titrations of Pu(VI) in mixed hydroxy-carbonate solutions intermediate between these limits have been completed to determine whether any mixed hydroxycarbonate species might exist, as Neck et al noted for the corresponding Np(V) system. Representative spectra for the titration of PuO_2^{2+} and of the triscarbonato complex with NaOH are shown in Figure 5. Though analysis is not as yet complete of these complex data sets, it appears that two previously unreported mixed hydroxycarbonate complexes, $PuO_2CO_3(OH)_2^{2-}$ and $PuO_2CO_3(OH)_3^{3-}$ might be present. These species contribute to Pu solubilization in the intermediate pH range wherein one might expect to see precipitation of $PuO_2(OH)_2$. These assignments and the calculated equilibrium constants remain tentative at present.

U(VI) is the only important oxidation state of uranium in solutions of importance in tank waste cleanup. Spectrophotometry is a comparatively less useful technique for describing U chemistry than it is in Np nd Pu chemistry, though the ion does fluoresce. In the present studies, ^{31}P, ^{13}C, and ^{17}O NMR spectroscopy, potentiometry and calorimetry have been employed as the principal analytical methods for characterizing U speciation in alkaline media. NMR spectroscopy indicates that uranyl complexes with oxalate and malonate (equimolar concentrations of uranyl and complexant) suppress uranyl hydrolysis up to pD ~ 8. At higher pD, oxalate was gradually released as free ligand due to the formation of $UO_2(OD)_x$ species. These results suggest that the available constants for U(VI)/oxalate complexation and U(VI) hydrolysis are applicable in predicting the U(VI)/oxalate complexation up to basic conditions. For the U(VI)/malonate system, these results do not establish at what pD malonate is unable to compete with hydroxide for UO_2^{2+}. However, the NMR results indicate that malonate is weaker and hydrolysis will become dominant at lower pD than in the oxalate system, again consistent with thermodynamic data from the literature.

Figure 5. Pu(VI) spectra demonstrating the appearance of new complexed species as $PuO_2^{2+}{}_{aq}$ or $PuO_2(CO_3)_3^{4-}$ are titrated with NaOH.

HEDPA was employed as an exploratory leachant during the earliest stages of this investigation. It has been noted that HEDPA is capable of dissolving MnO_2 from sludge simulant samples and simultaneously partially or completely (depending on the element) dissolving actinides. Organophosphorus complexants of this type are also known for their ability to both descale corroded surfaces (that is, dissolve metal oxides) and to passivate metallic surfaces against corrosion. To support possible utilization of this complexant for similar applications in tank waste cleanup, sludge dissolution, and residue stabilization, the same methodology used for studies of uranyl oxalate/malonate were continued to investigate the ligand/OH competition for HEDPA. The thermodynamics of actinide complexation by this chelating agent in acidic solutions has been described previously. Continuing studies indicate more complex behavior characterizes the actinide complexes formed in this system at elevated pH. Potentiometric (pH) and spectrophotometric titrations, combined with ^{31}P NMR spectroscopy and EXAFS experiments have confirmed the existence of multiple $M_mH_hL_l$ complexes across the pH 2-12 region, as shown in Figure 6. The complexes identified include ML, ML_2 and M_2L_2 species with
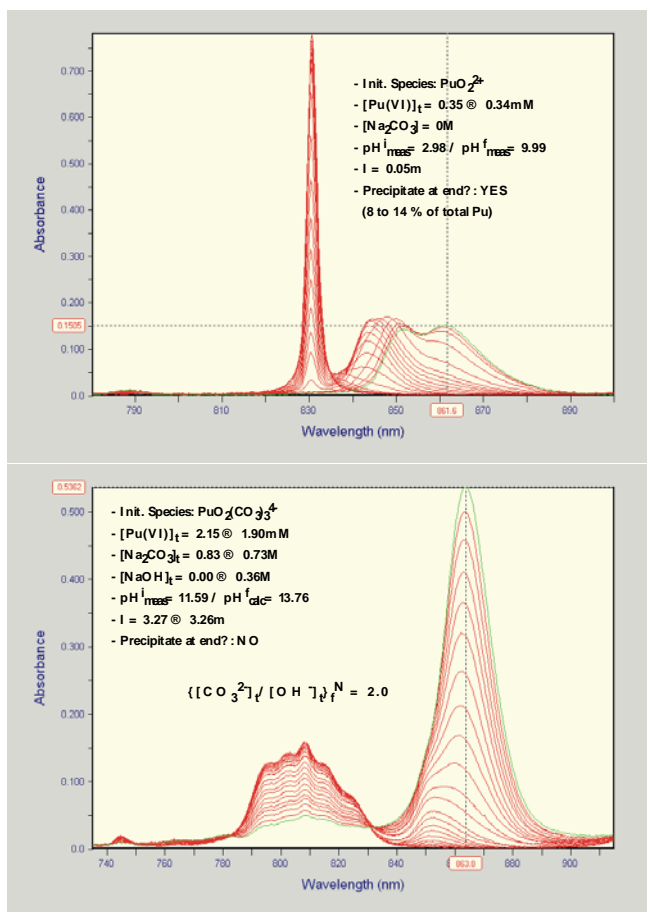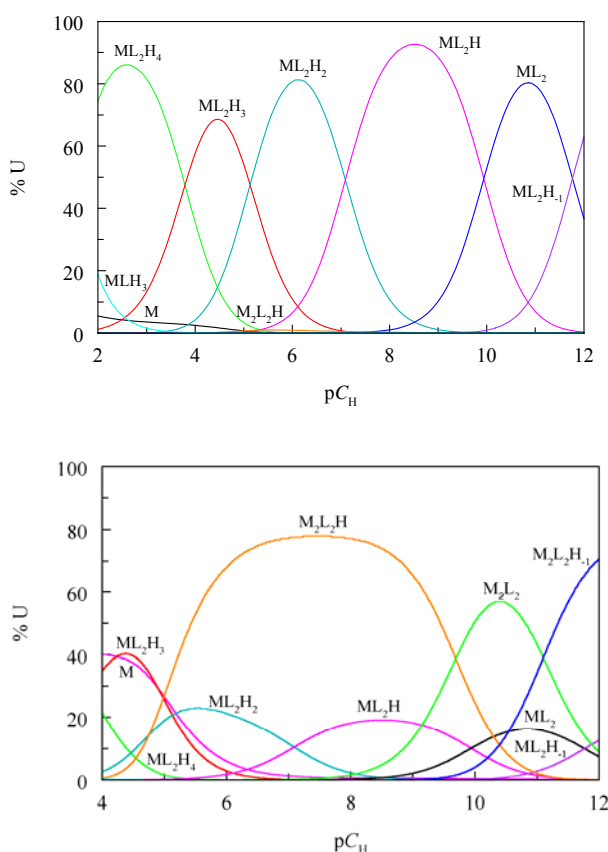
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Figure 6. a) Formation of U(VI)/HEDPA complexes as a function of pC_H. I = 1. 0 M tetramethylammonium chloride. C_U = 0.008 M, C_L = 0.016 M, LH_4 stands for the ligand HEDPA, b) Formation of U(VI)/HEDPA complexes as a function of pC_H. I = 1. 0 M tetramethylammonium chloride. C_U = 0.005 M, C_L = 0.006 M. LH_4 stands for the ligand HEDPA.

varying numbers of bound protons and hydroxide anions incorporated as well. Where they overlap, the equilibrium constants determined are generally consistent with previously reported data obtained by separations techniques in acidic solutions. It is known from previous investigations that diphosphonic acids are capable of maintaining U(VI) in solution over a wide range of pH. It has also been demonstrated that this complexant can be readily decomposed using Fenton-like chemistry to produce phosphate, CO_2 (or weakly complexing carboxylates) and H_2O.

Kinetics of actinide interactions with diphosphonate chelating agents. The rate of complexation between UO_2^{2+} and a few related diphosphonic acids, including HEDPA, VDPA (vinylidene-1,1-diphosphonic acid) and BZDPA (benzene-1,2-diphosphonic acid), was studied by stopped-flow absorption spectroscopy, using chlorophosphonazo III (CLIII) as the competing agent. Figure 7a shows the absorption spectra collected within 4 seconds of mixing a solution of U(VI)/CLIII and a solution of HEDPA. The peaks at 620 and 670 nm are due to the U(VI)/CLIII complex while the 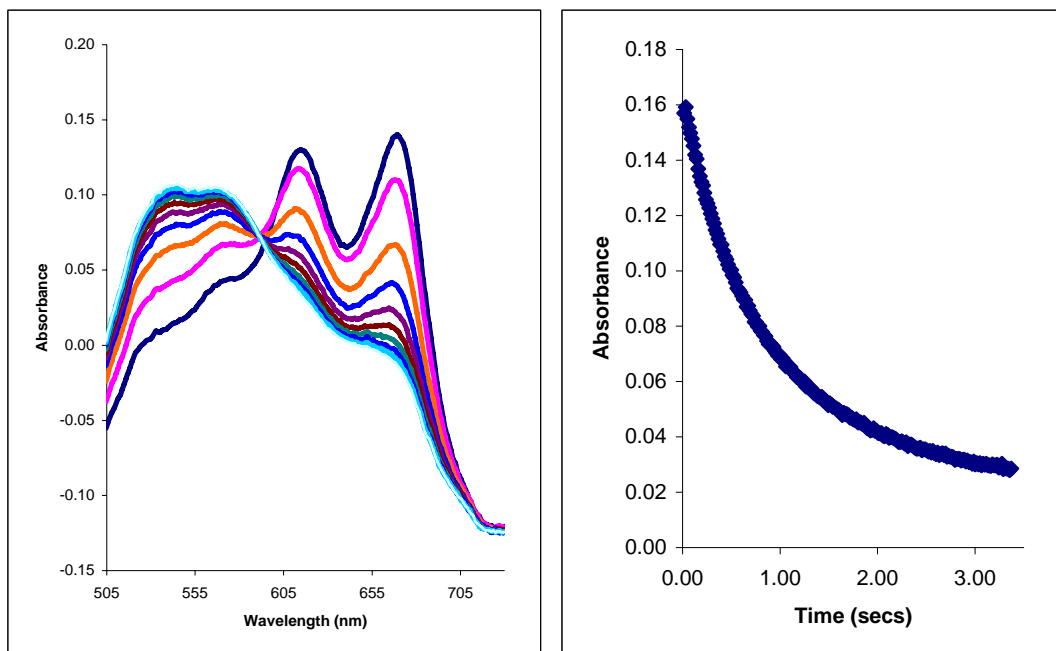broad bands at 520-570 nm are due to the free CLIII ligand. Upon mixing with HEDPA, the CLIII was freed due to the formation of U(VI)/HEDPA complexes. Figure 7b shows a kinetic trace at 610 nm. The stopped-flow experiments have been conducted at different pH and reactant concentrations. Global analysis of the sets of spectra as shown in Figure 7a generates the rate constants of the reaction and helps to reveal the reaction mechanism. Preliminary analysis of the data indicates that the reaction rate of U(VI) complexation with a few related diphosphonic acids follows the order: HEDPA > VDPA > BZDPA, which could be rationalized by the ligand rigidity and steric effect on the formation of U(VI) complexes.

Figure 7: *Stopped-flow absorption spectroscopy. [U(VI)/CLIII] = 0.00001 M; pH = 2; [HEDPA] = 0.005 M. (a) Absorption spectra at different time after mixing (t_{max} = 4 seconds); (b) kinetic trace at 610 nm.*

Boehmite leaching studies: Effect of HEDPA on the Sorption of Actinides on γ-alumina.

The nuclear waste sludges in underground tanks at Hanford contain most of the actinides as well as non-radioactive materials. Among these materials, aluminum oxide is particularly problematic to the vitrification of high-level waste sludges because it is present in large amounts and it is not as easily removed from the sludge by baseline leaching processes. The earlier exploratory leaching studies with sludge simulants indicated that HEDPA could assist with the dissolution of Al-oxides. Furthermore, interactions of actinides with aluminum oxide have significant implications in designing the strategies for sludge leaching. Therefore, the behavior of actinides in the leaching of aluminum oxide with HEDPA, a complexant that forms strong complexes with actinides and aluminum in acidic to basic solutions, has been investigated.

Batch adsorption/dissolution experiments were first conducted to examine the effect of HEDPA on the dissolution of aluminum oxyhydroxide boehmite (γ-AlOOH) in 1.0 M NaCl. As shown by Figure 8, in the pH range 4 to 9, complexation of Al by HEDPA significantly enhanced dissolution of boehmite. This phenomenon was especially pronounced in the neutral pH region where the solubility of aluminum is limited by the formation of sparsely soluble aluminum hydroxides. At higher pH, dissolution of boehmite appears to be slightly inhibited by HEDPA. Both enhancement and inhibition of boehmite dissolution are assumed to be due to differing modes of coordination between HEDPA and the boehmite surface. To help understand the interactions between HEDPA and aluminum oxyhydroxide, the Al(III)/HEDPA complexes in solutions were characterized by thermodynamic (potentiometry and calorimetry) and spectroscopic techniques (^{31}P and ^{27}Al NMR).
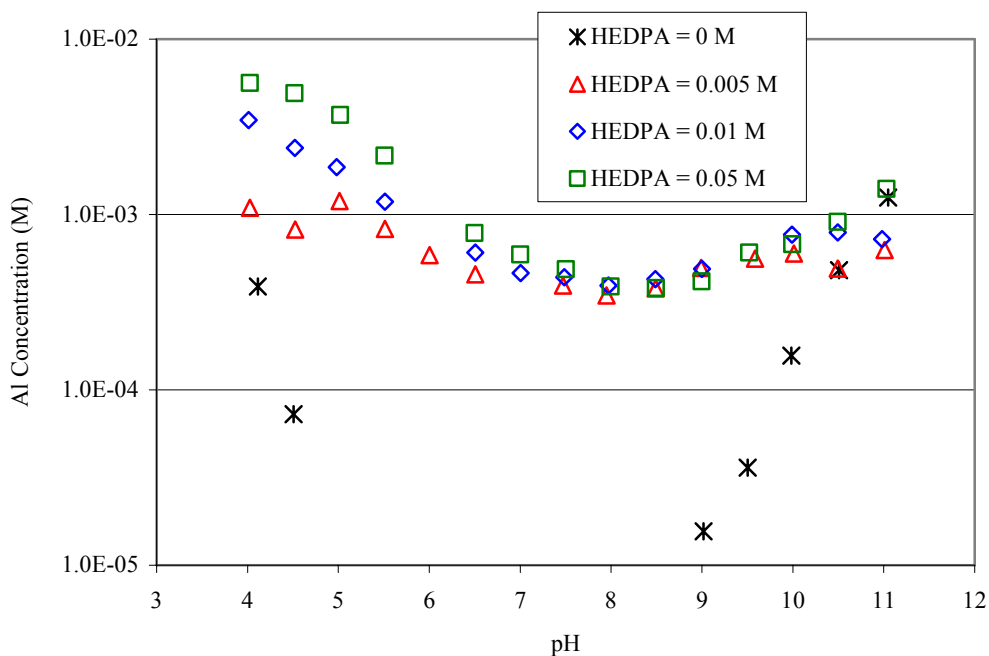
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Figure 8: *Effect of HEDPA on boehmite dissolution after 86 days (1.0 M NaCl; 0.01 M (0.60 g L^{-1}) boehmite)*

Uranyl Gluconate Chemistry

The suggestion has been made that organic complexants could be employed for selective leaching of Al/Cr species to enhance removal of matrix metal ions. One reagent that has been identified, gluconate (^-O_2C-$(CHOH)_4CH_2OH$), is of particular interest because it is known to strongly complex many different metal ions in alkaline solutions. Gluconate also is believed to be present in some wastes as a by-product of process application or of cellulose degradation. Though it is well known that polyvalent metal ions interact with gluconate, little information is available on the interactions of actinides with this ligand at high pH, ionic strength and temperature. The work presented here describes results of an investigation into the coordination chemistry UO_2^{2+} in relevant media. Selected highlights of this continuing work are described as follows:

- It has been suggested in the literature that the alcoholic protons in gluconate have measurable Brönsted acidity and thus can be readily lost from gluconate upon complexation. An investigation by ^{13}C NMR did not provide any compelling evidence for deprotonation of the alcoholic protons upon addition of up to 4.5 equivalents of base in samples containing only gluconate. This result implies that the alcoholic groups have pK$_a$'s above 13.

- Potentiometric titrations (Figure 10a) have been done to characterize the equilibria describing the complexation of uranyl by gluconate over the pH range of 3-12. The best fit of the potentiometric titration data required the presence of six species of the general stoichiometry $[(UO_2)_{1-2}(OH)_{2-5}(Gluc)_1]^{-2-0}$.

- Complex formation constants are reported as overall constants and are defined by the below equation and tabulated in Table 1.

$$\beta_{mhl} = \frac{\left[\left(UO_2^{2+}\right)_m (OH)_h L_l\right]\left[H^+\right]^h}{\left[UO_2^{2+}\right]^m [L]^l}$$

- The speciation of uranyl gluconate in the millimolar concentration range is complex and involves the formation of bimetallic complexes involving two uranyl cations associated with a single gluconate molecule.

- The results of a calorimetric investigation complemented by the results of a computational investigation of the uranyl-gluconate system suggest the possibility tha the $M_2(gluc)_1$ species may involve the complexation of dinuclear hydroxide-bridged uranyl dimers $(UO_2)_2(OH)_2^{2+})$. The computational results also suggest a significant role for hydrogen bonding interactions between the γ- or δ-hydroxide of gluconate with the uranyl oxygen atoms.

The predominance of species having the general stoichiometry $(UO_2)_2(OH)_{3-5}$gluc, that is multiple metal cations bound to a single ligand with only a single obvious chelation site (the α-hydroxycarboxylate end of the molecule), is the most notable feature of the system.
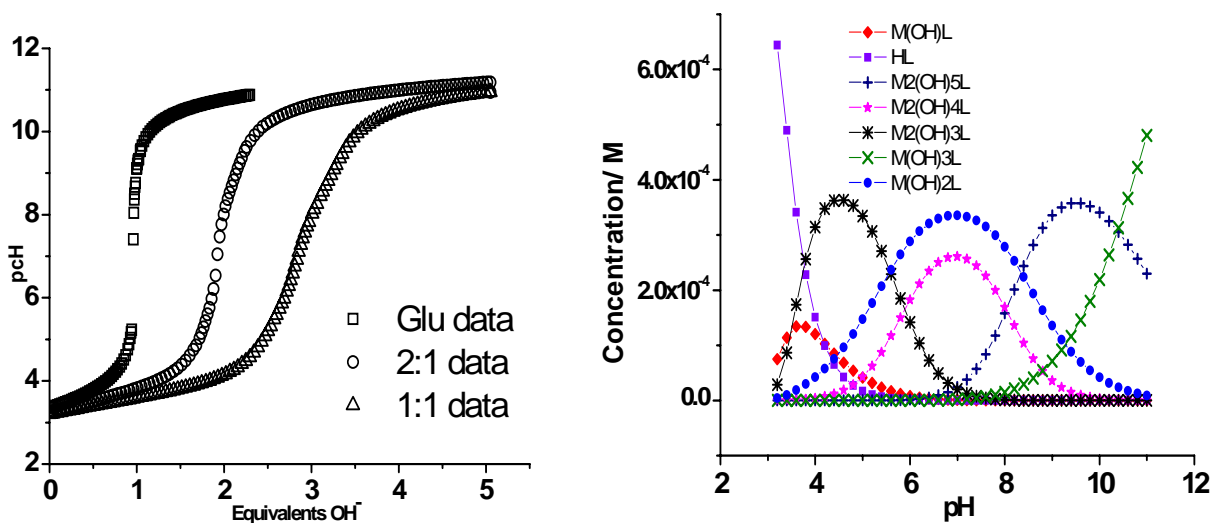

Figure 10 a. *pH titrations of sodium gluconate, a 2:1 mixture of Glu: U and a 1:1 mixture of Glu:U ([Glu]$_{init}$ = 0.001 M in each),* 10b. *Calculated speciation of uranyl gluconate at [UO$_2^{2+}$] = [NaGluc]$_t$ = 0.001 M.*

Table 1. *Stability constants of UO_2^{2+} with Gluconate for the complex $(UO_2^{2+})_m(H)_h(L)_l$ (I=0.1 (NaClO_4), 25 C).*

Stoichiometry mhl	$Log\beta_{mhl}$	$\pm 1\ \sigma$
1, -1, 1	-0.63	0.07
1, -2, 1	-5.08	0.03
1, -3, 1	-14.36	0.03
2, -3, 1	-4.35	0.03
2, -4, 1	-10.24	0.05
2, -5, 1	-18.27	0.04

Actinide removal from contaminated $Al(NO_3)_3$ by conventional separations methods: Cleanup of Aluminum Nitrate Solution by Solvent Extraction and Extraction Chromatography

Operational experience with actual sludge samples and simulants has established that aluminum removal by a straight-forward leaching with concentrated alkali achieves inconsistent degrees of success. The previous exploratory leaching studies suggest that contact of sludges (leached first with concentrated alkali) release substantially larger amounts of Al when a follow-on contact with dilute acid is applied. Application of acidic leachants for enhancing Al removal could improve Al waste management, but might at the same time encourage the release of additional TRUs from the sludge. As the actinides mobilized will never become the dominant species in these leachates, it appears that their removal from dissolved aluminum solutions should be a comparatively straightforward separations problem readily addressed by solvent extraction, extraction chromatography, or ion exchange. In the final stages of the final renewal project, the applicability of several materials/compounds that could removed trace amounts of TRU's from aluminum nitrate under a variety of conditions, including the presence of excess base and oxidants like permanganate or chromate were investigated. A variety of reagents/sorbents (including TBP, trioctylphosphine oxide, CMPO, and various commercially available resins) were tested for their ability to remove low concentrations of Pu, Am, U, and Np from $Al(NO_3)_3$. As Al is not redox active, actinide oxidation state adjustments can be made freely. Earlier results provide guidance as to which transition metals might be dissolved in parallel with the Al, thus requiring that accommodation be made (for example) for Fe to reduce its competition with the actinides. It has been observed that:

- 30% TBP in dodecane will effectively remove U from solutions containing high concentrations of $Al(NO_3)_3$, millimolar chromate and dilute nitric acid. Back extraction of the uranium is also readily accomplished by contact with dilute nitric acid, the level of decontamination is such that the $Al(NO_3)_3$ would be considered low-level wastes at worst.

- Chromium(VI) exhibits some tendency to partition into the organic phase in the absence of U(VI), a greater tendency to partition when U(VI) is present, and under some conditions resistance to back extraction. Contact of the organic solution containing

chromate with a reducing agent results in the removal of most of the chromate from the organic phase if enough time for contact is allowed.

- At higher concentrations and moderate levels of acidity, Cr(VI) is reduced in the presence of TBP. One hypothesis is that incomplete back extraction of Cr may well be the result of retention of Cr(III) species in the organic phase. Other studies indicate that $Cr(NO_3)_3$ is at best weakly extracted by 30% TBP, suggesting some hysteresis in the solvent extraction. At higher nitric acid concentrations, there is evidence for interfacial redox reactions. It appears that pre-application of a water soluble reducing agent accomplishes Cr(VI)-Cr(III) reduction and a cleaner separation of U(VI) from the $Al(NO_3)_3$ solution.

- The results indicate that 60% TBP in dodecane can remove >90% of both the Eu(III) (and by inference, trivalent actinides) and the UO_2^{2+} from HNO_3 solutions containing $Al(NO_3)_3$, though in the case of Eu^{3+} not uniformly. This observation is in general accord with previous reports on TBP extraction, though the particular combination of conditions studied in this program have not been previously reported. Decontamination of nitrate solutions by solvent extraction with 60% TBP is shown in Figure 11. Improved decontamination performance was seem using the same technique with the stronger extractant molecule, tri-(n-octyl)phosphine oxide (TOPO).

- TBP and TOPO have also demonstrated effectiveness in decontaminating nitrate solutions when deployed in extraction chromatographic mode. The partitioning of Eu(III) into the TBP-XAD7 and TOPO-XAD7 resin from solutions of constant [HNO_3] increased significantly with increasing [$Al(NO_3)_3$] over the $Al(NO_3)_3$ concentration range of 0.10 – 1.50 M. The highest value observed for both systems was at [HNO_3] = 0.01 M and [$Al(NO_3)_3$] = 1.5 M. This was somewhat expected since the competition between HNO_3 is minimized at lower acid concentrations and a large excess of nitrate is available for formation of the neutral europium/TBP adduct. Uptake behaviors for TBP and TOPO-XAD7 were determined as a function of increasing [$Al(NO_3)_3$] (0.010 M – 1.50 M) at three constant [HNO_3], and also for increasing [HNO_3] (0.01 M – 1.50 M) at two constant [$Al(NO_3)_3$].

The results for Eu^{3+} and UO_2^{2+} can be taken as generally representative of the behavior of trivalent and hexavalent actinide (and lanthanide) cations in a system of this type. A possible adjustment of this protocol that would certainly increase the efficiency of trivalent ion extraction would be to introduce a stronger extractant system, many of which are available. However, such adjustments would potentially lead to the increased removal of non-radioactive matrix ions, hence would have to be carefully considered. Fe(III), Mn(III), and Mn(IV) are important components that might have a significant impact in the deployment of a system modeled after this research.
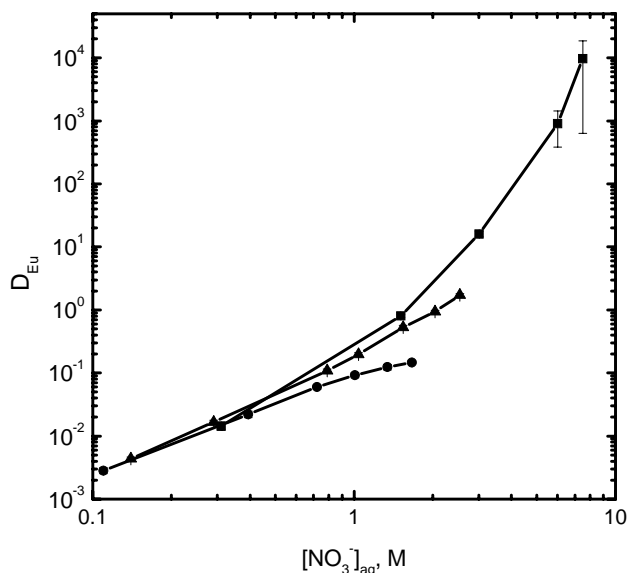
Figure 11: Extraction of $Eu(NO_3)_3$ into 60%TBP-dodecane from ▪ $Al(NO_3)_3$, ▲ $NaNO_3$, ● HNO_3. All solutions contained 0.01M of the non-varying electrolytes, 1.0 mM Cr(III), and excess ascorbic acid

The efficiency of vitrification processes and the volume of wastes that will ultimately be produced are significantly impacted by the large amounts of Al present <u>and</u> by the small amounts of $SO_4^=$, $CrO_4^=$, and PO_4^{3-} that are present in slurry feeds to the vitrifiers. Greater control of the transport of these species will enable the creation of more robust waste forms and more efficient processes for glass making. Preliminary work has been completed to establish the efficacy of heavy metal precipitation for anion control in sludge leachates. The objective of this aspect of the program was to precipitate these anions by addition of Ba^{2+}, Pb^{2+}, Cd^{2+}, (for $SO_4^=$ and $CrO_4^=$) or Ln^{3+},

Fe^{3+} (for PO_4^{3-}) solids for disposal as low-level wastes containing minimal radioactivity. Early results include non-radioactive scoping experiments in which small volumes of dilute $BaCl_2$ is mixed with dilute solutions of Na_2SO_4, Na_2CrO_4, or Na_3PO_4 as a function of pH followed by gravimetric analysis of the precipitates, and 24 hour precipitation and sorption experiments with $^{152,154}Eu$ tracer (as a model for An^{3+}). As shown in Figure 12, the expected near quantitative precipitation of $BaCrO_4$ and $BaSO_4$ effectively quantitatively removes these anions from dilute solutions over a wide range of pH, while Ba^{2+} has more limited success in controlling phosphate solubility. Eu sorption onto and removal from (or incorporation into) the solids is a complex function of conditions. These results establish the basic validity of the concept.
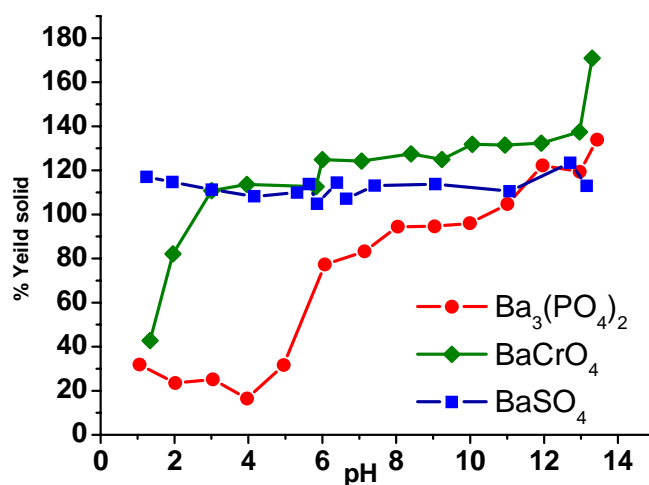

Figure 12. *Precipitation of $SO_4^=$, $CrO_4^=$, and PO_4^{3-} upon addition of $BaCl_2$ solutions.*

16

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J. C. Shafer, K. L. Nash
15th Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 21-25, 2007.

Workforce development contribution: The research personnel who have contributed to this project have found a variety of different positions, as follows:

Dr. Mark Jensen, Scientist, Chemical Science and Engineering Division, Argonne National Laboratory

Dr. Leigh Martin, Assistant Scientist, Actinide Separations Group, Idaho National Lab

Dr. Marion Borkowski, Staff Scientist, WIPP Project, Los Alamos National Lab, Carlsbad, NM

Dr. Ivan Laszak, Staff Scientist CEA, Saclay, France

Prof. Brian Powell, Assistant Professor, Environmental Science and Engineering Department, Clemson University

Dr. Artem Gelis, Engineer, Chemical Science and Engineering Division, Argonne National Laboratory

Dr. Alexander Garnov, Staff Member, Missouri University Research Reactor (MURR), University of Missouri, Columbia, MO

Dr. Andy Bond, Consultant, Andbeyond Enterprises (nuclear medicine interests)

Ms. Holly Hall, Pharm.D., practicing Pharmacist

Mr. Ryan Harrington, Chemist, Analytical Services, San Francisco, CA

Ms. Jenifer Shafer, Graduate Student, Washington State University

Mr. Ryan Witty, Radiological Technician, U.S. Navy, Bremerton Naval Shipyard, Bremerton, WA.

Mr. James Neeway, former Graduate Student, Radiochemistry, Oregon State University

Personnel who worked on this project whose current whereabouts are unknown: Melissa Hancock, Amanda Routt, Dr. Wendy Reed (was a postdoctoral associate at Los Alamos and Brookhaven National Labs)

Summary of Accomplishments

A number of correlations and fresh insights into the nature of the interactions between actinides, alkaline tank simulants, and reagents that could be useful for tank waste remediation have been developed:

1. It has been confirmed that comparatively little Pu or Am dissolves from any sludge type as a consequence of the baseline alkaline scrub though 10-30% of radiotracer U and Np can be mobilized from PUREX sludge into the 3.0 M NaOH scrub.

2. Results of exploratory sludge leaching with increasingly aggressive reagents (weak chelating agent, dilute acid, moderate acid, strong chelating agent) profile the dissolution of sludge matrix components. Considerable dissolution of Fe_2O_3 was noted in a dilute acid

wash of PUREX and Redox sludges. This removal was not always accompanied by extensive dissolution of actinides. The 2.0 M HNO_3 of sludges dissolved more Fe_2O_3, Cr_2O_3 and the lanthanide oxides/phosphates/fluorides from $BiPO_4$ sludges. The strong chelating agent (0.5 M HEDPA) wash dissolved MnO_2.

3. Aluminum dissolution behavior is far more complex, aluminum oxides dissolving most prominently in dilute nitric acid from the Redox sludge, but being released in increments of 10-30 % from PUREX sludge simulant as a result of the increasingly aggressive sludge leach procedures. No single treatment achieved complete Al mobilization from any of the sludge samples, though 2/3 of Al was leached from Redox sludge simulant using 0.1 M HNO_3

4. Oxidative leaching with permanganate or persulfate resulted in enhancement of Cr leaching through oxidation to the hexavalent state (in agreement with observations on real sludge samples), but with significant concomitant enhanced dissolution of both Pu and Am. The enhancement probably results from the combined effects of sludge matrix disruption and oxidation of the actinide ions. Permanganate reacts with some organic complexants to produce MnO_2 that retards Pu dissolution. Alkaline permanganate does not oxidize oxalate or citrate at room temperature but does consume edta, gluconate and glycolate.

5. Speciation studies of uranium in sludges and solutions indicate that polycarboxylate ligands (particularly oxalate) may compete with carbonate and hydroxide in the pH 2-8 range. EXAFS experiments of uranium in the sludge phase indicate that the uranium ions are in slightly different coordination environments in each sludge type. Thermodynamic parameters for the interaction of uranyl with the organophosphorus complexant HEDPA have been determined in support of possible future applications of such complexants for tank closure applications.

6. Electrochemical and spectrophotometric investigations of neptunium speciation in concentrated alkali indicate that the symmetrical hydroxides $NpO_2(OH)_4^{3-}$, $NpO_2(OH)_4^{2-}$, and $NpO_4(OH)_2^{3-}$ are the predominant Np(V), Np(VI), and Np(VII) species at base concentrations above 1.0 M (NaOH or LiOH). Mixed hydroxycarbonates of similar structures for Np(V) and Np(VI) are important in 1-3 M NaOH with 0.3 M Na_2CO_3 present, but no equivalent species is indicated for Np(VII). At base concentrations above 6 M the symmetrical hydroxides again appear to predominate. Similar observations are made for Pu speciation, but electrochemical reversibility (indicating similar coordination environments for the species in different oxidation states) is seen only at significantly higher base concentrations.

7. New mixed hydroxycarbonate complexes of Pu(VI) ($PuO_2CO_3(OH)_2^{2-}$ and $PuO_2CO_3(OH)_3^{3-}$) have been tentatively identified. These species may be important as bridge species between $PuO_2(CO_3)_3^{4-}$ and $PuO_2(OH)_4^{2-}$ species that dominate plutonium speciation at lower and higher pH values.

8. Cleanup of mildly acidic $Al(NO_3)_3$ solutions contaminated with small amounts of actinides and lanthanides can be decontaminated by the application of either solvent extraction or extraction chromatographic separation methods. The decontamination factors achievable with either technique are high enough to qualify the $Al(NO_3)_3$ for either recycling or low

level waste disposal, avoiding the need to incorporate this material in high level glass waste forms.

9. The diphosphonate complexing agent, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) significantly enhances the solubility of aluminum hydroxides. The degree of enhancement is dependent upon the bulk solution pH and the concentration of HEDPA. HEDPA can also leach uranium from synthetic boehmite through solid phase dissolution and/or the formation of U(VI):HEDPA complexes. Partitioning of uranium was observed to vary with pH and correlated with the partitioning of HEDPA and HEDPA-promoted boehmite dissolution. The sorption of uranium to boehmite in the presence of HEDPA is proposed to be through ternary U(VI):HEDPA surface complexes. These results indicate that HEDPA could be used to reduce the volume of the aluminum component of sludge within the Hanford waste tanks. However, at the circumneutral pH values examined in this work, the aluminum concentrations achieved during HEDPA leaching are several orders of magnitude too low to be of practical use. Furthermore, because a significant fraction of uranium (and presumably other actinides) could also be leached from boehmite by the addition of HEDPA, careful consideration of the partitioning of the actinides must be made if a strong complexant such as HEDPA is selected for sludge washing.

10. Finally, this project has directly contributed three new staff scientists to the ranks of the DOE National Labs (Borkowski, Martin, Guelis), two new academic radiochemistry experts (Powell, Garnov), one CEA scientist (Laszak) and several voters educated in the importance of nuclear and radiochemistry in modern society.