Project ID: **65398**

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

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CHARACTERIZATION OF ACTINIDES IN SIMULATED ALKALINE TANK WASTE SLUDGES AND LEACH SOLUTIONS

DOE Project Number 65398

No graduate students, two postdoctoral associates to join shortly

RESEARCH OBJECTIVE

Current plans call for an alkaline scrub of actinide-bearing sludges in the Hanford Waste tanks prior to their incorporation in glass waste forms. Though it is assumed that actinides will remain in the sludge phase during this procedure, this assumption is based on insufficient supporting thermodynamic and kinetic data. In this project we will investigate the fundamental chemistry of actinides in strongly alkaline solution and solid phases to strengthen the foundation and identify potential limitations of this approach. We will focus on the characterization of the leaching of actinides from simulated $BiPO_4$, REDOX, and PUREX sludges, the identification of actinide mineral phases in the sludge simulants, and the possible solubilization of actinides by complexation and radiolysis effects. This program will provide new fundamental information on the chemical behavior and speciation of uranium, neptunium, plutonium, and americium in simulated alkaline tank waste sludges and alkaline scrub liquors. Sludge simulants will be prepared from the appropriate matrix components using published data for guidance. Actinide ions will be introduced in the oxidation states pertinent to process conditions. We will characterize the speciation of the actinides in the sludges using a variety of techniques. In parallel studies, we will address the chemistry of actinide ions in alkaline solutions, principally those containing chelating agents. The third critical element of this research will be to assess the impact of radiolysis on actinide behavior. By correlating actinide speciation in the solid and solution phases with sludge composition, it will be possible to predict conditions favoring mobilization (or immobilization) of actinide ions during sludge washing. The new information will increase predictability of actinide behavior during tank sludge washing, and so contribute to minimization of the volume of high level waste created.

RESEARCH PROGRESS AND IMPLICATIONS

In the first eight months of this project (as of June 1, 1999), we have accomplished the following:

To augment the permanent staff investigators at our two institutions, we have conducted an extensive search for postdoctoral research candidates with expertise appropriate to the conduct of these experiments. Our respective searches (at LBNL and ANL) have identified two junior scientists from Russia with prior experience on the chemistry of actinides in strongly alkaline solutions. Dr. Garnov from the Russian Institute of Physical Chemistry of the Russian Academy of Sciences in Moscow will be joining the LBNL group during July, 1999. Dr. Guelis, from the same Institute has just completed his degree requirements in June, 1999 and will join the ANL group July 1, 1999. To fully enable planned investigations relying on electrochemistry, we have enlisted the assistance of Dr. Giselle Sandi of ANL and Professor Petr Vanysek of the Chemistry Department, Northern Illinois University. Addition of Professor Vanysek to our research team may offer an opportunity to incorporate graduate students into this research program.

We have prepared (at ANL) simulated sludges representative of those generated during operation of the $BiPO_4$, REDOX, and PUREX processes at Hanford between 1944-1986. Samples have been sent to LBNL. The LBNL group will focus on describing the behavior of Am and U while the ANL group emphasized Np and Pu. Non-radioactive samples are being subjected to various analyses to characterize the materials with respect to crystalline solids that are present. X-ray powder diffraction is the principal analytical technique being applied.

Samples of these sludges have been contacted with alkaline solutions containing plutonium in predominantly oxidized and reduced oxidation states. The radioactivity is, as expected, nearly quantitatively sorbed to the solid sludge samples. The solids have been contacted with solutions representative of the expected sludge washing protocol and with increasingly aggressive solutions. The latter leaches are designed to determine the strength with which the Pu is held by the sludge matrix, and potentially to reveal details about the chemical speciation of the Pu in the sludge phase. The results are summarized in the attached figure. For the most part, alkaline sludge washing procedures solubilize less than 5% of the Pu in these early tests. The more aggressive treatments do lead to the dissolution of Pu from the sludges. Additional experiments are planned with Am, U, and Np species sorbed to the sludges, and to examine the effects of thermal and radiolytic aging of the samples.

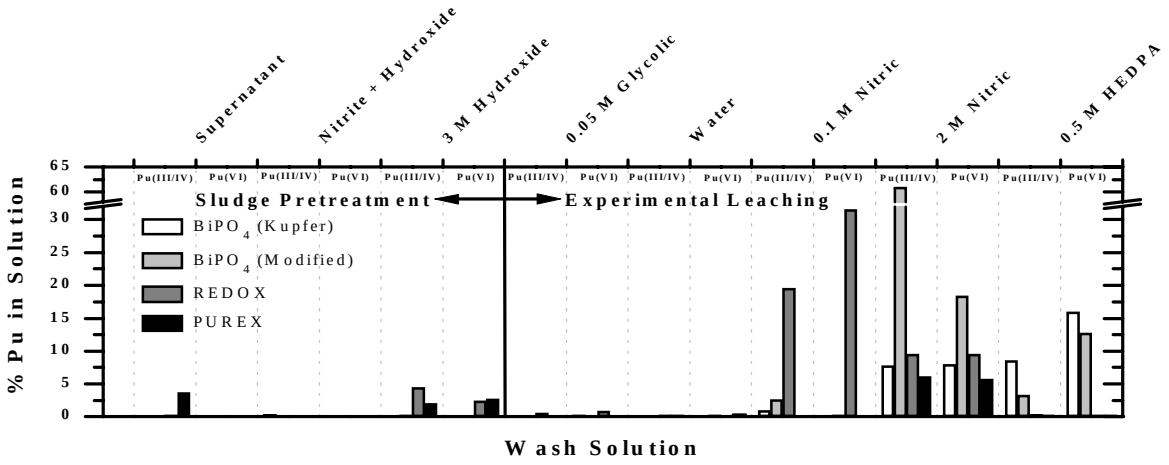
We have also made the qualitative observation that glycolic acid apparently solubilizes hexavalent (U(VI)) and pentavalent (Np(V)) actinides in concentrated alkali beyond the extent predicted by available thermodynamic data. We have completed the synthesis of a ^{13}C-labeled sample of glycolic acid for a planned NMR-based investigation of the kinetics of actinide-glycolate ligand exchange reactions.

PLANNED ACTIVITIES

Poster presentations are planned on this work for the 23rd Actinide Separations Conference, the American Chemical Society New Orleans meeting in the First Accomplishments of the EMSP Program symposium, and the Separation Science & Technology meeting in Gatlinburg in the fall. A proposal to do XANES/EXAFS experiments on the sludges has been submitted to SSRL for the LBNL portion of the work. Future experiments will address dissolution-redeposition processes during sludge washing using multiple isotopes of the same element (e.g., ^{239}Pu, ^{238}Pu, ^{242}Pu). We believe that colloid transport will be an issue of concern during sludge washing. This aspect of the system will be explicitly addressed. The next stage of the leaching experiments will include thermal and radiolytic "aging" of the samples. Leaching studies of sludges will identify which of the representative sludge surrogates have the greatest probability of actinide mobilization. Will follow this study with macro-actinide synthesis and diffraction studies to identify any crystalline actinide phases that may be present. As appropriate, actinide oxidation states in solids (after aging/radiolysis) will be identified spectrophotometrically or by XANES. Kinetics of actinide complexation reactions with glycolate, citrate, and EDTA fragments will be investigated by stopped-flow spectrophotometry and NMR spectroscopy. Electrochemical studies will commence as we complete our equipment setup and new personnel join the group.

Benefits of Research:

Achieving predictability in the speciation (oxidation states, complexation, solubility, and surface sorption characteristics) of actinide ions in strongly alkaline solutions and solids in contact with such solutions will aid significantly in ensuring reliable operation of the conversion of alkaline tank wastes to high level waste glass. Specifically, correlation of actinide speciation with the non-radioactive constituents of tank wastes will make it possible to identify a priori tanks in which actinide ions may dissolve as a result of sludge washing procedures.


Supernatant
Nitrite + Hydroxide
3 M Hydroxide
0.05 M Glycolic
Water
0.1 M Nitric
2 M Nitric
0.5 M HEDPA
Pu(III/IV)
Pu(VI)
Sludge Pretreatment
Experimental Leaching
BiPO4 (Kupfer)
BiPO4 (Modified)
REDOX
PUREX
% Pu in Solution
0
5
10
15
20
25
30
60
65
Wash Solution