Project ID: **59967**

Project Title: **Aqueous Electrochemical Mechanisms in Actinide Residue Processing**

DOE Report Number: 99-2911

Lead Principal Investigator:

Dr. David E. Morris
Technical Staff Member
Los Alamos National Laboratory
MS J586
P.O. Box 1663
Los Alamos, New Mexico 87545
Telephone: 505-665-6487
e-mail: demorris@lanl.gov

Co Principal Investigators:

Dr. Wayne H. Smith
Los Alamos National Laboratory
MS E510
P.O. Box 1663
Los Alamos New Mexico 87545
Telephone: 505-667-2365
e-mail: wsmith@lanl.gov

Dr. Carol J. Burns
Los Alamos National Laboratory
MS J514
P.O. Box 1663
Los Alamos New Mexico 87545
Telephone: 505-665-1765
e-mail:cjb@lanl.gov

Dr. David L. Blanchard Jr.
Senior Research Scientist
Pacific Northwest National Laboratory
P. O. Box 999
Richland Washington 99352
Telephone:
509-372-2248
e-mail: dl.blanchard@pnl.gov

Aqueous Electrochemical Mechanisms in Actinide Residue Processing

Mid-Year Progress Report

David E. Morris **Principal Investigator**
Carol J. Burns **Co-investigator**
Wayne H. Smith **Co-investigator**
David L. Blanchard, Jr. **Co-investigator**
Los Alamos National Laboratory
and
Pacific Northwest National Laboratory

LANL LAUR # 99-2911
June 1, 1999

Goals of Project:

New and/or improved solutions to the stabilization and volume reduction of nuclear materials processing residues are urgently needed. Mediated electrochemical oxidation / reduction (MEO/R) processes are one such approach for incinerator ash, combustibles, and other solid residues. However, questions remain concerning the mechanisms of these processes, and how they might be optimized. In addition, further research is merited to extend their range of applicability. Recent advances in the study of heterogeneous electron transfer in solid substrates have opened the door for the re-examination of electron transfer processes associated with redox mediated actinide dissolution. We will develop a deeper understanding of the thermodynamic and mechanistic aspects of heterogeneous electron transfer that lie at the heart of these MEO/R processes. We will also develop and test new approaches based on the results of these fundamental studies using actual residue materials. Key aspects of this proposal include:

- Determination of the potential windows for oxidation / reduction of colloidal actinide oxides and actinide-bearing oxide and organic substrates and the e^--transfer kinetic parameters that govern the current - overpotential characteristics.

- Development of adaptations of mediation schemes and application of co-mediation reagents for oxidative and reductive dissolution based on complexation of the surface-bound or solid-phase actinides and/or the dissolved redox mediator.
- Execution of bench-scale tests of new MEO/R schemes on actual residue materials.

Technical Description of Work:

Experimental studies must be directed at three principal goals. The first of these is the elucidation of the fundamental nature (i.e. both thermodynamic and kinetic parameters) of electron transfer between solution and solid species. These studies must determine the function of the electron transfer reagent, or catalyst, and must therefore examine both electrochemical (redox potentials) and physical (ion mobility in the substrate) factors. The second goal will be to evaluate the enhancement of dissolution rates as a function of dissolution promoters, or "co-catalysts". Finally, efforts will be directed at testing the viability of these hypotheses at larger scale. These studies must provide information relevant to a variety of substrate types, and to both uranium and plutonium-bearing materials. In order to accomplish this, it is necessary to study the influence of a number of variables, including substrate or matrix, electron transfer reagent, and co-catalysts or dissolution agents.

A. Systems & Substrates

Systems designed to reliably recover plutonium or uranium from residue materials must address the enhanced dissolution of both actinide oxides and actinides entrained in other matrices. In order to examine this variability, these investigations will examine three general classes of substrates: dispersed actinide solid phases, actinides sorbed to inorganic and organic colloids, and actinide-modified electrodes.

B. Electron Transfer Studies

Most electrochemical investigations will be carried out under acidic conditions in order to solubilize dissolved actinide ions, and to generate an electrochemical window in aqueous solution which provides access to as many potential electron transfer catalysts for oxidation of uranium and plutonium oxides as possible. Baseline studies will be conducted in the absence of catalysts to examine direct heterogeneous electron transfer between electrodes and the actinide-sorbed colloidal materials and between actinide-bearing overlayers and the underlying electrode surface materials. Standard voltammetric probes including cyclic voltammetry, chronoamperometry, and chronopotentiometry will be used with modifications as required to accommodate the heterogeneity of these systems. These studies will provide direct information on the potential windows for redox activity and the kinetics of the heterogeneous electron transfer to the actinide-bearing materials from which we can derive current (i.e., dissolution rate) - overpotential relationships for use in designing the most appropriate dissolved catalyst systems.

Subsequent studies will examine the activity of the most common mediators employed to assist the oxidation or reduction of metals and organics, including Ce^{4+}, Ag^{2+}, and Co^{3+}. These ions represent two different classes of activity: direct electron-transfer agents (Ce^{4+}, $E^o = +1.44$ V in 1 M H_2SO_4), and ions which are capable of oxidizing or reducing water and generating secondary redox-active species in solution (Ag^{2+}, $E^o = +1.98$ V; Co^{3+}, $E^o = +1.84$ V in 3 M HNO_3). While the latter class may prove more active, these ions will also be significantly less selective in their activity, and are likely of less utility in a process seeking to electrochemically “leach” actinides with minimal substrate degradation.

C. Perturbations from Complexation Chemistry

Investigations incorporating the addition of ancillary complexants to the bulk electrochemical system are intended to enhance the rate (and potentially the specificity) of actinide desorption/dissolution. The addition of ligands with high affinities for uranium or plutonium generally have the effect of complexing oxidized or reduced actinide species on the surface to enhance their solubility and speed the rate of dissolution. Hard acid ligands such as phosphates are likely to have the strongest affinity for actinyl ions in preference to lower oxidation state ions (An(IV) and An(III)). Reductive dissolution will likely be facilitated by the use of softer complexing agents (either multidentate, or containing softer donor sites) such as EDTA and TTA. Alternatively, ligands can be added which have the effect of complexing the catalytic electron transfer agent, and "tuning" its redox characteristics (generating species similar to the discrete metal complexes discussed previously).

D. Additional Methodologies and Probes

Many standard and advanced spectroscopic probes and surface characterization tools are being used to characterize surface interactions and surface chemistry, bulk speciation in reaction solutions, and interfacial processes during electron-transfer. Two specific spectroscopic investigations accompany nearly every experimental system, although they will not be applied to all experiment. These are (1) UV-Vis-NIR electronic spectroscopy (absorption, photoacoustic, and/or luminescence depending on the actinide, its oxidation state, and concentration) to determine the speciation of the dissolved actinides in solution, and (2) surface-sensitive molecular spectroscopies (x-ray absorption, optical luminescence, and/or Raman depending on actinide and oxidation state) to characterize the speciation of the actinide on the solid substrate before and after electron transfer / dissolution.

Routine analyses of the mediated electrochemical dissolution reactions are being conducted using standard analytical tools for uranium and plutonium assay. These include radiometric methods such as liquid scintillation counting, spectrophotometric methods including UV-Vis-NIR absorption and inductively-coupled plasma atomic emission spectroscopies, and electrochemical methods such as differential pulse stripping voltammetry and square-wave voltammetry. Solid-liquid phase separations by filtration and/or ultracentrifugation will precede all analyses. In general, the extent of dissolution of the actinide-bearing solid phase will be determined by measuring the actinide concentration in the electrolyte solution.

Accomplishments to Date:

This report summarizes work after 20 months of a 3-year project. Significant progress in the past calendar year has been made along several different research fronts. These include (1) preparation and characterization of uranium, plutonium and europium substrate-supported samples on SiO_2 and TiO_2, (2) electrochemical investigations of the reduction processes of the substrate bound UO_2^{2+} and Eu^{3+} samples, (3) electrochemical investigations of the effects of complexants/co-catalysts on the redox behavior of UO_2^{2+}, (3) x-ray absorption spectroscopic studies of neptunium, plutonium and surrogate metal bearing substrate samples, and (4) methods development in support of the project goals. In addition, mediated oxidation studies have been conducted on ion-exchange resins to assess the efficiency of the mediated process in destroying the organic substrate. Additional details in each of these areas is provided below.

A. Preparation and Characterization of Sorption Samples.

Sorption studies have been performed utilizing both TiO_2 and SiO_2 as substrates. Initial experiments were performed using uranium (UO_2^{2+}) and europium (Eu^{3+}) as model ions. A series of experiments has also been performed with Pu^{4+} as the sorbing species. Stock solutions of these ions (at concentrations between 150 and 600 ppm) were prepared at pH values between 1 and 7, and these solutions were contacted with the inorganic substrates. The substrates were subsequently reisolated by centrifugation or ultrafiltration, and the concentration of metal ions in solution measured by inductively coupled plasma - atomic emission spectroscopy (ICP-AES). In general, it was observed that both substrates were effective sorbants in the pH ranges investigated. In general, there was little variability in the sorption of europium as a function of pH, whereas in the case of uranium, sorption was found to be slightly better at higher pH values. These results suggest that the Eu^{3+} is associating with the surfaces via outer-sphere mechanisms, whereas the UO_2^{2+} ion is forming inner-sphere surface complexes. These results are consistent with existing literature on the uptake of metals on metal oxide surfaces. It was also observed that a small but identifiable amount of leaching/dissolution of the substrates occurred. In particular, it was found at higher pH values that up to 10 ppm titanium could be identified in the post-contact solutions. The presence of these ions in significant quantities could significantly impact the redox characteristics of the solutions.

Bulk quantities of these sorption samples were also prepared under similar conditions to provide sufficient material for spectroscopic characterization and for the electrochemical investigations described below. Spectroscopic characterization was conducted for both Eu^{3+} and UO_2^{2+}-laden SiO_2 and TiO_2 using time-resolved optical luminescence spectroscopy. The luminescence spectra obtained for Eu^{3+} on the SiO_2 substrate are very similar to those obtained in low pH aqueous solution. This again suggests that the metal is associating with this surface via an outer-sphere mechanism. For the Eu^{3+}/TiO_2 sample there is a substantial change in the luminescence spectrum relative to the dissolved hydrated species. New bands are observed in the spectra that are consistent with new surface species and the existing bands show changes in relative intensity. These results may indicate that there are multiple sorption complexes on this substrate. The UO_2^{2+}/SiO_2 sorption samples yielded luminescence spectral data quite similar to that observed previously in our labs. These data a wholly consistent with the inner-sphere surface complexation mechanism. The UO_2^{2+}/TiO_2 samples did not give rise to a luminescence spectrum. These samples are known to be subject to photochemical reactivity and it is possible that the luminescence is being strongly quenched by the photochemical processes although there was no noticeable degradation of the sample. Additional studies are underway.

B. Electrochemical Investigations

The initial voltammetric studies of the substrate-bound Eu^{3+} samples (both SiO_2 and TiO_2) showed clear evidence for release of the metal from the surface under the action of supporting electrolyte solution. This is expected for outer-sphere complexes since the electrolyte effectively out-competes the Eu^{3+} ions for the surface sites. However, the voltammograms also showed evidence of an additional electroactive Eu^{3+} species that is likely to be the surface-bound material. This additional voltammetric wave occurs ~ 100 mV more negative that the reduction wave for the dissolved Eu^{3+} species, but the peak position is not strongly scan-rate dependent. Thus, the peak shift likely reflects the thermodynamic rather than kinetic behavior of the surface-bound metal. Notable, this implies that the surface-bound species is more difficult to reduce than the dissolved species. Additional experiments with these materials are underway and results will be reported shortly.

The influence of complexing anions on the redox properties of dissolved UO_2^{2+} were investigated using the bidentate ligands carbonate and acetate and the monodentate ligands hydroxide and chloride. Extremely large cathodic potential shifts were observed for the carbonate and hydroxide systems: nearly 1 V in each case. The acetate and chloride ligands perturb the redox potential by only tens to hundreds of millivolts. An equally interesting observation, however, was the change in the electron-transfer kinetics as a function of metal complexation. The measured rate constant for electron transfer varied by a factor of 30,000. The acetate complex was nearly classically reversible and therefore had the fastest rate whereas the carbonate complex had a very sluggish electron-transfer rate. Because there is no correlation between redox potential and electron-transfer rate, this finding points to the importance of determining both thermodynamic and kinetic factors in these systems to properly optimize the mediated metal dissolution. For example, a system in which the redox potential is favorable for mediated dissolution will have little practical value if the rate of electron-transfer across the interface is exceedingly slow.

C. XAS Structural Characterization of Samples

The French have used malonamides [R_2-N-(CO)-(CH_2)-(CO)-N-R_2] for extraction of Am, Eu and Cm trivalent ions from PUREX reprocessing waste streams. These types of compounds have been extensively studied recently, and have been shown to be effective for extraction of +4 actinide ions. The malonamides generally are not as effective as phosphate based extractants, such as CMPO. However, they have the distinct advantage of being easily thermally decomposed to produce relatively innocuous waste products (H_2O, CO_2, and NO_x) and avoiding formation of phosphates that degrade glass quality. We have investigated the structure of tetramethyl malonamide [TMMA, $(CH_3)_2$-N-(CO)-(CH_2)-(CO)-N-$(CH_3)_2$] and tetramethyl succinamide [TMSA, $(CH_3)_2$-N-(CO)-(CH_2)-(CH_2)-(CO)-N-$(CH_3)_2$] complexes of Nd(III) in acetonitrile in preparation for the investigation of similar Pu complexes.

Nd(III) forms $Nd(NO_3)_3$ï2TMMA and $(Nd(NO_3)_3)_2$ï3TMSA crystals, and their structures have been determined by single crystal XRD. The Nd is 10 and 9 coordinate in the TMMA and TMSA crystal structures, respectively. The TMMA molecules are bidentate - both oxygens of both TMMA molecules coordinate one Nd ion. One TMSA molecule of the Nd-TMSA complex is bidentate, while a second TMSA coordinates two adjacent Nd ions, one with each of its oxygens. This effectively forms a bridge linking the two Nd ions, and gives rise to the 2:3 ratio of Nd to TMSA.

Extraction data, however, suggest that in solution, at high complexant to metal ion ratios, both complexants form 1:3 complexes - one Nd ion to 3 complexant ions - indicating structures very different from those in the crystals. The most obvious explanation for the difference is that the complexants are binding in a monodentate fashion. However, analogous (monodentate) amides are much worse extractants than the malonamides and succinamides, suggesting that this is not the case. Another explanation is that the Nd ion is capable of coordination by 12 ligands. This is not a very satisfying explanation either, since there is no compelling reason to expect such a change in coordination. Another explanation is that the solution complexes have some unusual structure in which, for example, one of the complexants is associated with the Nd, but removed to essentially an outer sphere position, or one or more of the nitrates are monodentate, etc. An explanation on the basis of such structures is also fairly unsatisfying, since it seems doubtful that an uncharged complexant (TMMA or TMSA) would be bound strongly enough in an outer sphere position to remain associated with the complex, or that an oxygen ligand on an (uncharged) complexant could force out and replace one of the oxygen ligands from a (charged) nitrate ion.

We have used X-ray Absorption Spectroscopy (XAS) to study the structure of these complexes in solution in an effort to resolve this seeming contradiction between extraction data and expected solution structure. From the Extended X-ray Absorption Fine Structure (EXAFS) of three different solutions of $Nd(NO_3)_3$ and TMMA in acetonitrile , we find the ratio of Nd to TMMA in the solutions are 1:2, 1:6, and 1:10. There are clear changes in the EXAFS in the region above 7 _$^{-1}$ that indicate possible changes in coordination. Similar changes in the Nd-TMSA complexes in solution with increasing complexant to metal ratio are also observed. The EXAFS of these solutions are currently being fit to determine the structure of these complexes and the reasons for the observed differences.

D. Supporting Methods Development Work

A very important aspect of the proposed work is highly accurate and precise determinations of redox potentials (~ 1-2 mV precision) to properly measure stability constants for surface complexes and metal complexes. This presents serious challenges with existing commercially-available reference electrodes. In particular, reference electrode potentials drift due to changes in liquid junction as a result of differing ion migration rates in strongly acidic media. Furthermore, precipitation of salts occurs at the interface between the reference electrode and the test solution as a consequence of exceeding salt solubility in strongly ionic media. Finally, the outer electrode filling solution must contain an ion that will not form a complex with metals such as plutonium since it is in contact with test solution. To circumvent these problems an new reference electrode was designed and tested. The new design replaces the conventional fill solutions (KCl and KNO3) with perchlorate solutions.

Another important capability for this project is the determination of voltammetric data for Pu under dilute solution conditions. Even in relatively acidic solutions (e.g., pH 0 to 1) plutonium is only sparingly soluble. Thus, highly sensitive voltammetric methods must be employed. To this end, calibration curves for Pu in 0.1 and 0.092 M acid solution using square wave voltammetry on a platinum electrode have been constructed for use in the analyses of sorption samples. The results look very promising with a concentration range from 20 to 200 ppm and a lower detection limit of ~10 ppm. The next step will be to analyze solutions from prior experiments on the uptake of Pu on silica and alumina.

E. Mediated Dissolution Studies on Ion-Exchange Resins

One aspect of this project is to determine the dissolution kinetics of plutonium species entrained on the surface of solid materials. An example of a solid material that is ubiquitous throughout the nuclear complex is spent ion exchange resin that is used in plutonium recovery operations. These resin materials gradually lose their efficacy, presumably due to radiation damage from the absorbed actinide elements. This radiation damage can significantly alter the structure of the resin through free radical bond cleavage and recombination. In some cases the elements absorbed on the resin may become encapsulated and no longer available for elution. The mediated electrochemical oxidation process is capable of destroying the resinís organic matrix and liberating the encapsulated metallic ions. Part of this work was devoted to an investigation of the kinetics of the destruction of an industry standard cation exchange resin using three electron transfer mediators, cobalt(III), silver(II) and cerium(IV), in both nitric and sulfuric acid media. The goal of this study was to determine the conditions for optimum reaction efficiency.

The complete oxidation of a sulfonated styrene unit of a standard cation exchange resin proceeds according to reaction 1:

$$C_8H_8SO_3H \text{ ñ } 41\ e^- + 17\ H_2O \rightarrow 8\ CO_2 + SO_4^{2-} + 43\ H^+ \qquad \text{(Eqn.1)}$$

Each of the resin destruction experiments was run at a current of 1 ampere for 3 hours, a quantity of electricity sufficient to destroy approximately 0.51 grams of resin at 100 percent current efficiency. The average loss in weight of the resin was approximately 2-3 percent, verifying the chemically inert nature of this material even at elevated temperatures in strongly oxidizing nitric acid solution.

The oxidizing power of the three mediators chosen increases in the order Ce(IV)<Ag(II)<Co(III). At room temperature the disappearance of resin from the solution follows this same trend. With cerium(IV) there is essentially no reaction. Using silver(II) or cobalt(III) as mediator at 0.1 M concentration, the reaction proceeds smoothly, with the amount of resin destroyed exceeding the theoretical amount possible based solely on the number of coulombs of electricity passed. Two possible explanations exist for this behavior. First, the resin may not react completely to produce carbon dioxide, but instead form a water soluble intermediate. However, when a deficiency of

resin is used instead of an excess, analysis of the resulting solution typically gives results in the order of 100 ppm total dissolved organic carbon. Thus the reaction will proceed to completion. A second possible explanation is that while the resin itself is resistant to chemical attack by the strongly oxidizing nitric acid media, the intermediate products generated are not.

When the temperature is raised to 50 °C, the resin destruction efficiency using silver(II) and cobalt(III) as mediators is slightly greater than at room temperature, but the solution never develops the characteristic colors associated with the ions in their higher oxidation states. Two reactions are occurring simultaneously, reaction of the mediator with the resin and reaction of the mediator with solvent, as given in equation 2.

$$2\ H_2O + 4\ Co^{3+} \rightarrow O_2 + 4\ Co^{2+} + 4\ H^+ \qquad \text{(Eqn.2)}$$

The former reaction is expected to proceed at a faster rate at elevated temperatures, but the latter reaction, which also proceeds at a faster rate, lowers the effective mediator concentration. Thus raising the temperature appears to have little effect on the resin destruction rate. If the temperature is raised still further, to 70 °C and 90 °C, the resin destruction efficiencies with silver and cobalt gradually decrease. The deleterious solvent/mediator reaction rate begins to exceed that of the mediator/resin reaction.

The efficiency of resin destruction using cerium(IV) as mediator increases dramatically as the temperature is raised. From essentially an immeasurably low reaction at room temperature it increases to greater than 100% destruction efficiency at 50 °C, comparable to the efficiency observed with silver(II). At 70 °C, the efficiency approaches a phenomenal 400%, far exceeding either cobalt(III) or silver(II). At 90 °C, the efficiency ceases to increase signaling the onset of the solvent reaction with cerium(IV).

Trends observed in sulfuric acid media mimic those seen in nitric acid but in less dramatic fashion. With cobalt(III) as mediator there is a slight gradual decrease in destruction efficiency as the temperature is raised. With cerium(IV) there is essentially no reaction at room temperature but a steady increase in reaction efficiency with increasing temperature. Destruction efficiency in excess of 100 percent of theoretical is not observed with either mediator. This observation lends further validity to the assumption that nitric acid contributes to the oxidation process while the non-oxidizing sulfuric acid does not.

Experiments to measure the reaction kinetics and stoichiometry were carried out using cerium(IV) in nitric acid. Cerium(IV) was chosen due to its stability in aqueous solution at moderate temperatures while both cobalt(III) and silver(II) are not. In these experiments the cerium(IV) concentration was monitored spectrophotometrically with time following addition of resin. When a deficiency of resin was used the change in absorbance was used to calculate the quantity of cerium(IV) necessary to completely oxidize a given weight of resin. The average value obtained for three runs at 52 °C was 18.5 equivalents of cerium(IV) per equivalent of resin. The value is considerably lower than the theoretical value of 41 equivalents. Yet analysis for total organic carbon demonstrated essentially no soluble organic material remaining in solution.

Projections:

Fiscal Year 1999(remaining): (a) Complete voltammetric studies of Eu^{3+}, UO_2^{2+}, and Pu^{4+} sorption samples on SiO_2 and TiO_2. (b) Begin heterogeneous electron transfer studies with colloidal materials and dissolved-phase redox mediators. (c) Begin studies of ligand-catalyzed redox dissolution of metals on solid supports.

Fiscal Year 2000: (a) Complete heterogeneous electron transfer studies with these colloidal materials using potentiostatically-controlled metallic electrodes. (b) Continue heterogeneous electron transfer studies with colloidal materials and dissolved-phase redox mediators. (c) Conduct studies of the effects of actinide complexing agents (surface and dissolved) on dissolution using metallic electrodes and dissolved redox mediators. (d) Conduct solution speciation and surface complexation studies of reactant systems with and without actinide complexants. (e) Initiate scale-up studies of new mediator systems using incinerator ash as the residue stream.

Funding:

The FY 99 allocation for this project was \$ 250 K (\$ 190 K at Los Alamos and \$ 60 K at Pacific Northwest National Laboratory). Year to date expenditures have been ~ \$ 150 K and are consistent with planned spending rates. The remaining budget will be 100 % costed by the end of the fiscal year and project goals will be met with this budget.

Issues/Problems:

There are presently no significant issues or problems impacting the work on this project.

Corrective Actions:

Not applicable.

Additional Information:

Results from this project were presented at two national meetings during the past calendar year: the DOE Environmental Management Science Program Scientific Workshop in Chicago, IL on July 27-30, 1998 and in a presentation titled “Trends in Actinyl Electrochemistry: Voltammetry and Theory” which was presented at the 217th National Meeting of the American Chemical Society in Anaheim, CA on April 21-25, 1999. An additional paper titled “Aqueous Electrochemical Mechanisms in Mediated Dissolution of Actinide Residues” has been accepted for presentation in the forthcoming symposium First Accomplishments of Environmental Management Science Program scheduled for the 218th National Meeting of the American Chemical Society to be held in New Orleans, LA on August 22-26, 1999.

This project is also supporting a summer undergraduate research assistant during this fiscal year. The student, Ms. Tammy Diaz, is an environmental geology major at New Mexico Highlands University.