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Project Title: Aqueous Electrochemical Mechanisms in Actinide Residue Processing

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Research Objectives:

New and/or improved solutions to stabilization and volume reduction of nuclear materials processing residues are urgently needed. Mediated electrochemical oxidation / reduction (ME/OR) processes are one 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. 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.

Research Progress and Implications:

This report summarizes work after ~ 2.3 years of a 3 year project. The emphasis is on significant progress made in the past 12 months as described in detail in the Information Access items listed below. These new results have led to a presentation at a national meeting of the American Chemical Society and a manuscript accepted for publication.

Our research focus continues to be on the redox kinetics and energetics of UO_2^{2+} and Eu^{3+} (as a Pu surrogate) sorbed onto metal oxide phases that are constituents in incinerator ash residue. Detailed sorption studies versus pH and ionic strength have clearly shown that the sorption mechanism for both metals entails inner-sphere complexation. The strength of this interaction is greater for uranyl than europium on both substrates and greater for both metals on titania than on silica. Surface complexation has also been characterized by luminescence spectroscopic studies of the supernate and solid phases resulting from the sorption reactions. These data show significant differences in the spectral characteristics of the surface-bound metals relative to the metal species in solution in the equilibrium reactions. In

particular, for the Eu^{3+} surface complexes the hypersensitive transition in the emission spectrum shifts in a manner consistent with lowering of the symmetry of the metal ion as a result of the perturbing influence of the inner-sphere surface interactions. In addition, the emission lifetime for these Eu^{3+} surface complexes decreases in a manner consistent with the replacement of inner-sphere coordinated H_2O with surface hydroxyl groups. Similar results were obtained for the UO_2^{2+} surface complexes. Finally, the sorption samples were also subjected to heating at $\sim 200\text{ }^\circ\text{C}$ to mimic calcination. The impact on the surface speciation was significant. In effect, the variation in surface speciation seen with pH for the hydrated samples was removed, and all samples exhibited \sim constant surface complexation characteristic of intimate interaction between the metal species and the surface.

Voltammetric data have also been obtained for aqueous suspensions of the Eu^{3+} - and UO_2^{2+} -laden silica and titania samples. All data were collected at a static mercury drop electrode using a linear potential sweep method. The redox characteristics of these surface-supported analytes show a number of perturbations relative to the dissolved metal species in similar solutions. Both strong and weak sorption interactions of the colloidal material with the Hg electrode surface have been identified. The electrode sorption is stronger for the titania substrates than the silica. Surprisingly, however, the potential for substrate-bound metal reduction is not dramatically changed from what is observed in homogeneous solution. One of the more interesting observations from this work relates to the electron-transfer dynamics for the dehydrated samples. The dehydrated $\text{Eu}^{3+}/\text{SiO}_2$ sample actually shows faster electron-transfer than does Eu^{3+} in bulk homogeneous solution. In contrast, dehydrated $\text{UO}_2^{2+}/\text{SiO}_2$ shows slightly slower electron-transfer dynamics than UO_2^{2+} in bulk homogeneous solution. This behavior is almost certainly related to the nature of the interaction of the metal ions with the metal-oxide surfaces. However, since Pu^{4+} is expected to have a chemically similar surface complexation environment to that of Eu^{3+} , this result suggests that plutonium should also have more favorable electron-transfer kinetic properties on the residue surface than in bulk solution. Initial experiments have also been conducted in the presence of several simple complexing agents including acetate and carbonate. These results are still under analysis.

Planned Activities:

The remainder of this aspect of the project will be devoted to a comparable suite of experiments using the aluminous phase gibbsite and to further investigations of the role of homogeneous complexants on the dissolution/redox properties of the substrate-bound metals. The studies with gibbsite are intended to broaden the impact of this work to include solids isolated from HLW tanks at Hanford and Savannah River which include substantial solid aluminum phases. Other ongoing efforts supported at Los Alamos and by our PNNL collaborator include studies of MEO dissolution of organic substrates, voltammetric detection of plutonium at dilute concentrations, and spectroscopic (principally x-ray absorption) characterization of actinide chelate complexes.

Information Access:

Refereed Publications: “ Eu^{3+} and UO_2^{2+} Surface Complexes on SiO_2 and TiO_2 ,” T.A. Diaz, D.S. Ehler, C.J. Burns, and D.E. Morris, First Accomplishments of the DOE Environmental Management Science Program, American Chemical Society, **in press**.

Presentations: “Aqueous Electrochemical Mechanisms In Mediated Dissolution Of Actinide Residues,” D.E. Morris, C.J. Burns, W.H. Smith, D.L. Blanchard, and T. Diaz, Abstracts Of Papers Of The American Chemical Society, v. 218(pt.1) pp. 91-NUCL AUG 22, 1999

Optional Information:

Ms Tammy Diaz, a senior environmental geology major at New Mexico Highlands University who did a summer research internship in FY99 working on this EMSP project, was awarded a U. S. Department of Energy 1999-2000 DOE Environmental Management Scholarship Program Hispanic Scholarship Fund grant.