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Aqueous Electrochemical Mechanisms in Actinide Residue Processing

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Research Objective

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

Research Progress and Implications

This report summarizes work after 8 months of a 3-year project. Progress to date falls into three categories as discussed below:

Materials and equipment procurement: A new computer-controlled potentiostat was procured and tested for work with solid and Hg electrodes. A consensus was established among investigators regarding the metal-oxide substrates to be used in the initial phase of this project for actinide sorption and electrochemical characterization. TiO₂ and SiO₂ were selected and these materials were procured. Manufacturer characterization data have been compiled and in-house characterization (e.g., powder XRD) has been undertaken. Computer codes for digital simulations of electrochemical response functions have also been upgraded and ported into desk-top applications.

Detailed literature investigations: Background information was compiled on key experimental parameters for sorption and desorption studies, including selection of substrate and examination of surface physical characteristics. Although TiO₂ may be prepared by a variety of methods, its surface composition, structure and pH_{pzc} (5.6-6.5) do not vary significantly. Some literature reports of uranium (UO₂²⁺) uptake on titania have appeared, which suggest that sorption increases as a function of pH below pH 5-6, and then drops off at higher pH values. While little is known about the possible modification of surfaces with organic species (e.g., complexants), it is known that inorganic ions (e.g., PO₄³⁻, SO₄²⁻) may be absorbed under certain conditions, and TiO₂ will sorb CO₂ through a range of pH conditions. These anion effects have been demonstrated to alter metal uptake profiles.

Another variable is the redox potential of possible mediators. There are reports that the potential of the Ce(IV/III) couple may be altered significantly by counterion. For instance, the oxidation potential of Ce(III) can vary from +1.7 V (vs. NHE) in 1M HClO₄ to +1.4 V in 1M H₂SO₄. Upon coordination by stronger donor ligands a significant cathodic shift in redox potential may be observed. This effect has been employed to stabilize Ce(IV) in certain coordination environments, and the oxidation potential can be shifted by as much as 1 V. For organic complexants, redox potentials can also be "tuned" by variation of substituents. For instance, in a series of N,N'-ethylenebis(salicylidene-amine) ligands shifts in the Ce(IV/III) couple of 250 mV can be induced by variation of a single substituent. There is less evidence that simple complexants can be used to control the redox potential of other ions commonly used in mediated electrochemical reactions (e.g. Ag²⁺, Co³⁺). It is possible, however, to synthesize organometallic or inorganic coordination complexes of these ions with favorable redox characteristics. For instance, a series of substituted Ag(II) porphyrin complexes may be readily oxidized on either the spectroelectrochemical or chemical time scale without demetallation. Similarly, the cobaltocene (Co(C₅H₅)₂)/cobaltocenium redox couple is commonly employed in redox reactions in non-aqueous media; adaptation of this reagent to aqueous solution is possible through sulfonation of the carbocyclic ligand.

Preliminary results: One aspect of this work is the determination of formation constants between complexing agents and both dissolved actinide elements and electron transfer mediators. A standard way to obtain this information involves the precise measurement of shifts in electrochemical potential with addition of the complexant. Accuracy is critically dependent on a stable reference electrode. The highly acidic media necessary for some parts of this project precludes the use of standard reference electrodes, such as Ag/AgCl and saturated calomel, due to the constantly changing liquid junction potential and the precipitation of salts at the reference electrode-test solution interface. To overcome this problem we tested several reference electrode combinations, finally settling on a modified silver-silver chloride double junction electrode for use in strongly acidic, perchloric acid based media. The electrode consists of a Ag metal in contact with an internal filling solution of 5.0 M sodium perchlorate and 0.1 M silver perchlorate. A porous membrane connects this solution to an outer filling solution containing 5.0 M sodium perchlorate. Studies on the complexation of iron(II) and iron(III) with chloride in varying concentrations of perchloric acid demonstrated the required stability and accuracy of this reference electrode system.

Preliminary studies have been undertaken to determine the range of redox potentials and heterogeneous electron-transfer kinetic parameters for U(VI/V) and other uranium redox transformations as a function of solution conditions (1 M acid to 3 M base) and coordination environments (CO₃²⁻, EDTA, etc.). Over this acid/base range the U(VI/V) redox couple shifts from ~ -0.1 V vs Ag/AgCl to ~ -1.0 V. The e⁻-transfer rate constant (k₀) likewise changes from fast (immeasurable by voltammetry) in acid to slow (~ 0.005 cm/s) in concentrated base. Coordination of UO₂²⁺ by ligands other than H₂O or OH⁻ moves the U(VI/V) couple to values intermediate between acid and base regimes and there is substantial variability in the e⁻-transfer kinetics.

X-ray absorption spectroscopy (XAS) spectra of plutonium (Pu) in PuO₂, in a borosilicate waste glass simulant, and in calcined Rocky Flats ash were collected at the Stanford Synchrotron Radiation Laboratory. Plutonium in the glass and the ash is present as Pu(IV), and exhibits the PuO₂ structure. The Pu(IV) oxide in the glass exhibits significantly reduced order relative to the PuO₂ reference material. In contrast, the oxide in the ash is extremely well ordered, indicating that calcination of Pu loaded ash effectively converts all Pu to PuO₂, without formation of solid solutions with other oxides.

Planned Activities

Fiscal Year 1998(remaining): (a) Complete sorption experiments of actinides with SiO₂ and TiO₂. Characterize these solid phases by spectroscopy and microscopy. (b) Conduct heterogeneous electron transfer studies with these colloidal materials using potentiostatically-controlled metallic electrodes. (c) Begin heterogeneous electron transfer studies with colloidal materials and dissolved-phase redox mediators.

Fiscal Year 1999: (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.