

EMSP Project 82773 Annual Progress Report
Reporting Period: Jun 1, 2002 - May 31, 2003
Project Title: Contaminant-Organic Complexes: Their Structure and Energetics in Surface Decontamination Processes

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Research Objective

The current debate over possible decontamination processes for DOE facilities is centered on disparate decontamination problems, but the key contaminants (Thorium [Th], uranium [U], and plutonium [Pu]) are universally important. Innovative agents used alone or in conjunction with traditional processes can increase the potential to reclaim for future use some these valuable resources or at the least decontaminate the metal surfaces to allow disposal as nonradioactive, nonhazardous material. This debate underscores several important issues: 1) regardless of the decontamination scenario, metal (Fe, U, Pu, Np) oxide film removal from the surface is central to decontamination; and 2) simultaneous oxide dissolution and sequestration of actinide contaminants against re-adsorption to a clean metal surface will influence the efficacy of a process or agent and its cost. Current research is investigating the use of microbial siderophores (chelates) to solubilize actinides (i.e., Th, U, Pu) from the surface of Fe oxide surfaces. Continuing research integrates 1) studies of macroscopic dissolution/desorption of common actinide (IV) [Th, U, Pu, Np] solids and species sorbed to and incorporated into Fe oxides, 2) molecular spectroscopy (FTIR, Raman, XAS), to probe the structure and bonding of contaminants, siderophores and their functional moieties, and how these change with the chemical environment, 3) and molecular mechanics and electronic structure calculations to design model siderophore compounds to test and extend the MM3 model.

Research Progress and Implications

Research progress over the year from June 2002 to May 31, 2003 is reported. This report focuses on the work conducted at PNNL, but annual reports from participating institutions are presented under their individual grants; University of California, Merced grant award DE-FG07-98ER14926, and Princeton University grant award DE-FG07-01ER63283. Over the life of these investigations, the project has supported or is supporting three post-Doc positions at PNNL and University of California, Merced and two graduate students at University of California, Merced, and Princeton University. A listing of published or submitted journal articles and presentations arising from this project during the current reporting period are presented.

Thorium is a tetravalent ion that is a good analog to the tetravalent actinides U(IV), Pu(IV), or Np(IV), its solubility in 0.1 M NaNO₃ is approximately 5×10^{-3} M to 5.5×10^{-5} M from pH 3 to 5, respectively. Th(IV) adsorption to hematite, for the conditions utilized, increased rapidly from 0% sorbed to 100% sorbed over the pH range 3 to 4.0. After adsorption, two different hydroxamates (routotrillic acid [RA], and desferrioxamine B [DFB]) were utilized to desorb the Th and dissolve hematite. The rates of desorption and dissolution were studied as a function of time, hydroxamates type, and aging of the Th-hematite surface complex. Results from these studies show that sorbed Th is fully solubilized by both siderophores. However, the RA exhibits a faster rate of solubilization than the trihydroxamate, DFB.

Aging Th on the surface of hematite prior to desorption with RA or DFB, Th desorption rate, and the amount desorbed are decreased substantially; both the rate and amount of desorption appears to be inversely related to aging time (Figure 1). These results suggest that hematite-surface sorbed Th is a mononuclear inner-sphere complex that is homogeneously distributed over the Lewis acid sites of the hematite surface, but with aging time Th is either incorporated into the oxide structure do to continual

recrystallization of the hematite, or Th surface speciation shifts to a more polynuclear-like species, or surface precipitate of Th oxide. However, previous research suggests that a contaminant's ionic radius is the primary determining factor on contaminant incorporation due to recrystallization. The ionic radii of Th is approximately 1.02 angstroms, which is almost double that of the center metal ($\text{Fe}^{3+} = 0.64 \text{ \AA}$). Because of this difference in ionic radii, the results observed with aging are probably related to surface polymerization of Th. This question will be addressed through the interrogation of Th sorbed hematite (aged for various times) via XAS.

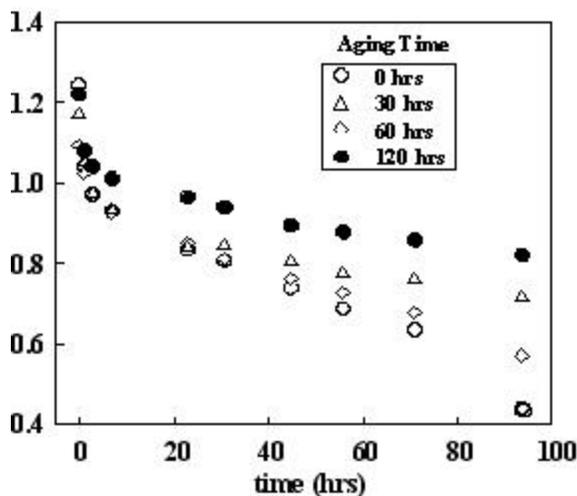


Figure 1. Effect of aging of Th on desorption from hematite by DFB.

Investigations of the extent of chelate (RA) induced dissolution of actinide oxides, and estimation of contaminant-siderophore complex stability have been completed during this reporting period. The specific objectives were: 1) to estimate the effect of RA in ThO_2 (am) solubility; 2) to estimate the stability of the Th-RA aqueous complexes formed under different pH regimes, and in the presence of different RA concentrations; and 3) to develop a thermodynamic model for the solubility of thorium oxide in the system: ThO_2 (am) – RA – Na – Cl at room temperature. These objectives were addressed through a series of pH-stat equilibration experiments using ThO_2 (am) as the actinide oxide specimen. The data generated from these experiments is being thermodynamically modeled using the Pitzer ion-interaction formalism to reproduce ThO_2 (am) solubility in dilute to concentrated NaCl solutions at 25 °C. A coupled, non-linear, least squares and chemical equilibrium

program (INSIGHT) is being used to calculate complexation constants for the Th-siderophore aqueous complexes and to calculate the ThO_2 (am) solubility constants in the presence of RA.

An extended MM3 model has been developed for Fe(III) complexes with catecholamides. Assignment of Fe-O stretch, Fe-O-C bend, and Fe-O-C-C torsion parameters was based on geometries and potential energy surfaces from density functional theory calculations, crystal structure data, and were investigated at the MP2 level of theory. These included rotational potential surfaces for several C-C bond types and hydrogen bonds involving phenol. The resulting model empirical relationships between force constants and physical properties. In addition to these metal-dependent interactions, several unknown intra-ligand interactions reproduce crystal structures with the expected level of accuracy. By changing only the M-O stretching parameters, a good agreement between calculation and experiment is obtained for other metal ions. In addition, we have found that this model is applicable to tropolonate complexes. Published barriers to octahedral inversion are reproduced to within ± 2 kcal/mol for $[\text{Al(III)}(\text{tropolonate})_3]$ and $[\text{Ga(III)}(\text{catecholamide})_3]^{3-}$.

Application of this model has led to the first quantitative structure-activity relationship for catecholamide ligands. Conformational searches yielded the lowest energy forms of the six-protonated ligands. Conformational searches were also run to identify the lowest energy forms of their Fe(III) complexes. We obtained the difference in steric energy between the Fe-L complex and the hexaprotonated ligand. A plot of pFe vs this energy difference yields the linear correlation (Figure 2). This result suggests that this method can be used to screen candidate architectures for ligands based on the catecholamide donor group.

Planned Activities

Dr. Ben Hay is currently collaborating with Prof. Kenneth N. Raymond, Department of Chemistry, University of California - Berkeley, providing computer-aided host design to assist with the discovery of improved metal ion sequestering agents. Currently laboratory experiments on solubilization of Pu(IV)O_2 and U(IV)O_2 by the hydroxamic acids discussed above are being planned. These studies will be coordinated with colleagues at Princeton University and University of California, Merced.

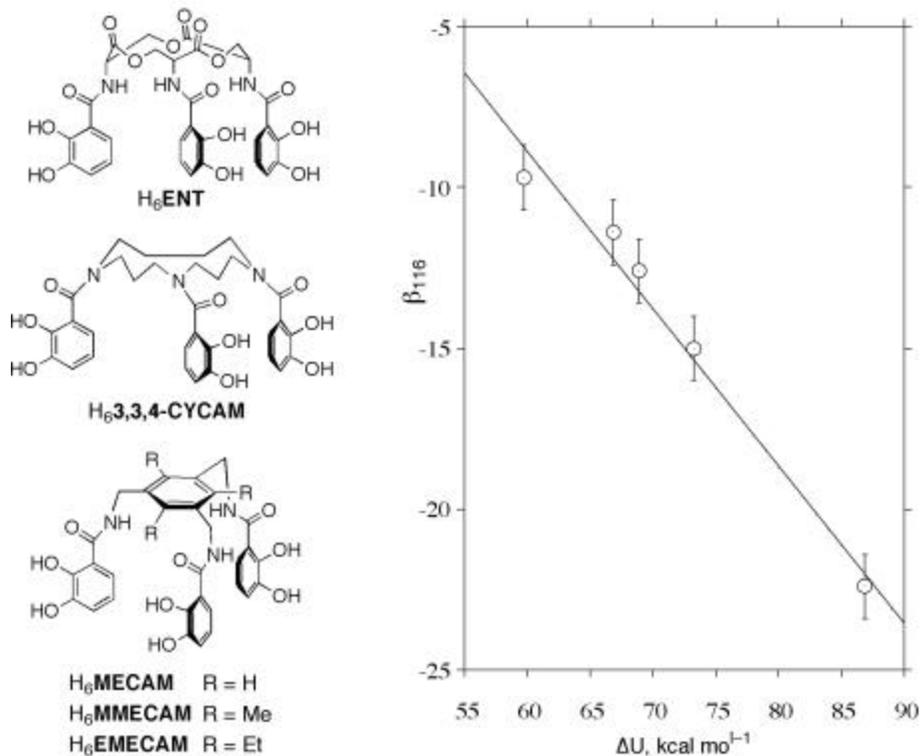


Figure 2. Plot of correlation between $\log K_{116}$ and ΔU (calculated difference in steric energy between the Fe(III) complex and the fully protonated ligand in their lowest energy conformations).

Publications and Presentations (since June, 2002)

Bluhm, M., B. P. Hay, S. K. Sangoo, E. A. Dertz, and K. N. Raymond. 2002. Corynebactin and a serine trilactone based analogue - chirality and molecular modeling of ferric complexes." *Inorg. Chem.* 41:5475-5478.

Ainsworth, C. C. and K. Wagon. 2003. Th(IV) desorption from hematite in the presence of di- and tri-hydroxamate siderophores: effect of aging. to be submitted to *Geochimica et Cosmochimica Acta*.

Qafoku, N. P., C. C. Ainsworth, D. Rai, and D. A. Moore. 2003. Amorphous ThO₂ solubility and Th-siderophore (rhodotorulic acid) aqueous complex stability in the Na⁺ - Cl⁻ - OH⁻ - H₂O system at room temperature. In preparation, to be submitted to *Radiochim Acta*.

Ainsworth, C. C., N. Qafoku, and K. Wagon. 2003. Aging effects on siderophore assisted desorption of Th(IV) sorbed to the surface of hematite. To be presented at the 226th ACS National Meeting, September 7-11, 2003 in New York, NY.

Uddin, J. and B.P. Hay. 2003. The computer-aided design of receptors for tetravalent actinides. 225th American Chemical Society National Meeting in New Orleans, Louisiana, March 2003.

Uddin, J. and B.P. Hay. 2002. Computer-aided design of actinide receptors containing catecholate chelate rings., abstract submitted to the Inorganic Poster Session, 224th American Chemical Society National Meeting in Boston, Mass, August 2002.