

**Title:** Chemical Speciation of Americium, Curium and Selected Tetravalent Actinides in High Level Waste.

**Project Number:** 26753

**Name of Laboratory:** Pacific Northwest National Laboratory

**PNNL Principal Investigator:** ANDREW R. FELMY

### **Problem Statement and Research Objective**

Large volumes of high-level waste (HLW) currently stored in tanks at DOE sites contain both sludges and supernatants. The sludges are composed of insoluble precipitates of actinides, radioactive fission products, and nonradioactive components. The supernatants are alkaline carbonate solutions, which can contain soluble actinides, fission products, metal ions, and high concentrations of major electrolytes including sodium hydroxide, nitrate, nitrite, phosphate, carbonate, aluminate, sulfate, and organic complexants. The organic complexants include several compounds that can form strong aqueous complexes with actinide species and fission products including ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), citrate, glycolate, gluconate, and degradation products, formate and oxalate.

The goal of this project is to develop aqueous thermodynamic models for organic complexants in tank waste and to use these models in chemical engineering applications at Hanford and other DOE sites.

### **Research Progress and Implications**

In FY05, we completed our thermodynamic models of tetravalent actinide-chelate complexation and initiated studies to model the effects of oxalic acid in tank wastes. Oxalic acid has either been used, or is currently being considered for use, at both the Hanford and Savannah River sites to remove sludges from the double shell tanks. An accurate thermodynamic model for the influence of oxalic acid on tank waste dissolution is therefore needed to help maximize the efficiency of potential oxalic acid additions.

### **Development of an Accurate Thermodynamic Model for Oxalic Acid Interactions with the Major Electrolytes.**

In this research we are developing an accurate aqueous thermodynamic model for the principal monovalent (Na), divalent (Ca, Mn, Sr, ..) cations in the HLW tanks and the important anionic components (Cl, NO<sub>3</sub>, SO<sub>4</sub>, PO<sub>4</sub>) at 25<sup>0</sup>C. The model is parameterized over the entire range of pH values from very acid (pH <1) to high pH (>10) and across a wide range of ionic strengths. The majority of the data for model parameterization was taken from literature sources. However, as part of this study, the solubilities for important solid phases (calcium and strontium oxalates)

were determined if the results were either unknown in the literature or the experimental data too uncertain.

The development began by determining the parameters for the neutral oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4(\text{aq})$ ) species from data in acid solutions and then extending the model systematically to include the bioxalate ( $\text{HC}_2\text{O}_4^-$ ) species and finally oxalate ( $\text{C}_2\text{O}_4^{2-}$ ). In many cases the determining the parameters for the bioxalate and oxalate species required refitting apparent equilibrium constant data in a thermodynamically consistent fashion with our oxalic acid parameters. Once the dominant electrolyte interactions with  $\text{Na}^+$  and the important anions were determined, we also included the necessary data for the divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Sr}^{2+}$ ). These cations were selected since they are either important in the initial tank wastes or have been found in the tank residuals following oxalic acid treatment ( $\text{MnC}_2\text{O}_4(\text{s})$  and  $\text{SrC}_2\text{O}_4(\text{s})$ ).

### Extension of the thermodynamic model to treat Al(III).

One of the principal components of the Hanford double shell tank sludges is aluminum. In fact oxalic acid additions to tank C-106 at Hanford resulted in almost half of the added oxalic acid being tied up with Al(III) species as a result of the dissolution of aluminum oxides. Therefore, an accurate thermodynamic model for the important Al(III)-oxalate complexes was required under acid conditions ( $\text{pH} < 4$ ).

The important aluminium-oxalate species include the monomeric  $\text{AlL}_n^{3-2n}$  ( $n=1-3$ ) species below pH 4-5 and at least two different polymeric hydroxo-oxalate complexes above these values. Given the diversity of aluminium-oxalate species and the range of formal charges, the ionic strength dependence of the speciation of these species cannot be confidently extrapolated to infinite dilution nor to brines from values derived at only one ionic strength. Equilibrium measurements were therefore carried out on the  $\text{H}^+$ - $\text{Al}^{3+}$ -Oxalate system as well as the  $\text{H}^+$ -oxalate and  $\text{H}^+$ - $\text{Al}^{3+}$  subsystems in ionic strengths ranging from 0.1 to 5 mol  $\text{dm}^{-3}$  NaCl at 298.15 K to provide a set of self-consistent conditional stability constants that can in turn be used to calibrate a Pitzer ion-interaction model capable of predicting the extent of aluminium-oxalate complexation in a wide range of ionic strengths. Examples of such measurements are shown in Fig. 1. A manuscript is currently in preparation summarizing these results.

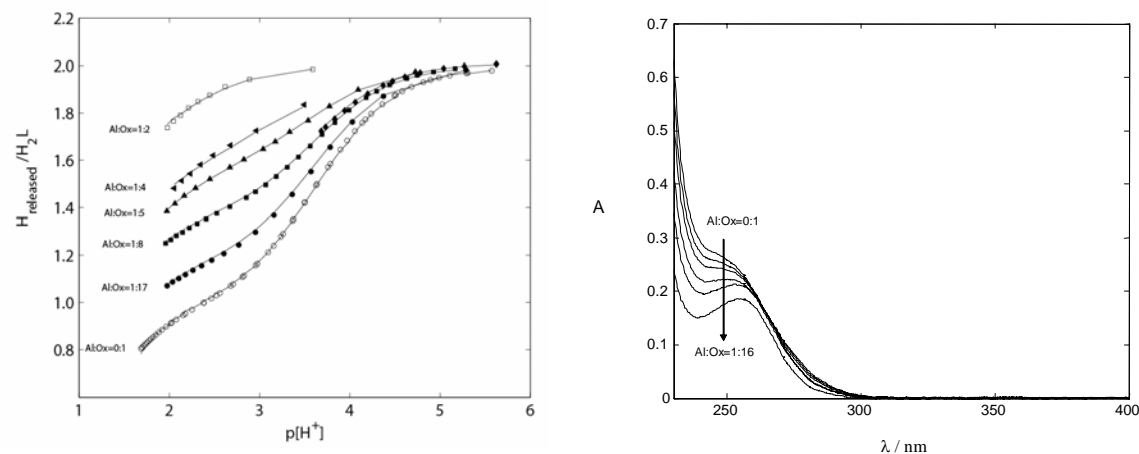


Fig 1a Potentiometric titrations in 3 mol dm<sup>-3</sup> NaCl at 298.15 K. Lines are fits from best-fitting model.

Fig 1b. Ultraviolet spectra of aluminium-oxalate in 5 mol dm<sup>-3</sup> NaCl (pH=1.55).

## **Publications**

Felmy, A.R., H. Cho, D.A. Dixon, Y. Xia, N.J. Hess, and Z. Wang. (2004). “Stoichiometry and Structure of Aqueous Thorium Citrate Complexes under Neutral to Basic Conditions.” Radiochimica Acta (in review).

Felmy, A.R., M. Mason, O. Qafoku, and D.A. Dixon. (2005). “Development of Accurate Chemical Equilibrium Models for the Hanford Waste Tanks: The System Na-Ca-Sr-OH-CO<sub>3</sub>-NO<sub>3</sub>-EDTA-HEDTA-H<sub>2</sub>O from 25 to 75 °C.” ACS Symposium Series 904, Subsurface Contamination Remediation, Accomplishments of the Environmental Management Science Program (E. Berkey and T. Zachary Eds.).

Felmy, A.R. and O. Qafoku. (2004). “An Aqueous Thermodynamic Model for the Complexation of Nickel with EDTA Valid to High Base Concentration.” Journal of Solution Chemistry 33(9):1161-1180.

Felmy, A.R., Z. Wang, D.A. Dixon, and N.J. Hess (2004). Chemical Equilibrium Modeling of Hanford Waste Tank Processing: Applications of Fundamental Science. In *Waste Management 04 Symposium. Basic Environmental Science Issues for D&D, ER and Long-Term Stewardship in the US*.

## **Other Contributions**

Dr. Felmy was also asked to serve as the Hanford site – EMSP HLW coordinator.