

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 determine the effects of hydrolysis, carbonate complexation, and metal ion displacement on trivalent and selected tetravalent actinide speciation in the presence of organic chelates present in tank waste and to use these data to develop accurate predictive thermodynamic models for use in chemical engineering applications at Hanford and other DOE sites.

Research Progress and Implications

In FY03, we completed our model on Sr complexation for the Hanford waste tanks and the majority of the studies on chelate complexation of the trivalent actinides to high ionic strength. The experimental studies now focus on the tetravalent actinides. Specifically, experimental studies were completed on Th(IV) with citrate, and gluconate. In addition, studies were also completed on EDTA complexation of the metal ion Ni(II), which can react with EDTA and inhibit actinide element complexation.

Each of these activities is described in the following sections:

Th (IV) – Citrate Complexation

Citrate is one of the principal organic chelates found in the Hanford waste tanks. However, only a few studies have examined the complexation reactions of citrate with tetravalent actinides under basic conditions. These earlier studies have focused on thermodynamic measurements of complexation reactions via solvent extraction, EMF or other techniques. Unfortunately, little

spectroscopic information was obtained to verify the identity of the complexes proposed from the thermodynamic measurements. In our study we have examined the Th(IV) citrate complexes in solution using NMR, XAS, molecular simulation and thermodynamic measurements (solubility). The results have shown the presence of previously unidentified species under basic conditions that dominate the aqueous complexation. Specifically, the ^{13}C NMR studies (Figure 1) show the presence of Th(IV)-citrate complexes with two and three citrate ligands bound to the asymmetric carboxylic acid and the adjacent α -hydroxyl. The molecular simulations of these complexes indicate that the α -hydroxyl proton is removed creating species of high charge (i.e., $\text{Th}(\text{Cit})_3^{8-}$ or possibly $\text{Th}(\text{Cit})_2\text{OH}^{5-}$). Thermodynamic data for the formation of these species has been determined from the solubility studies.

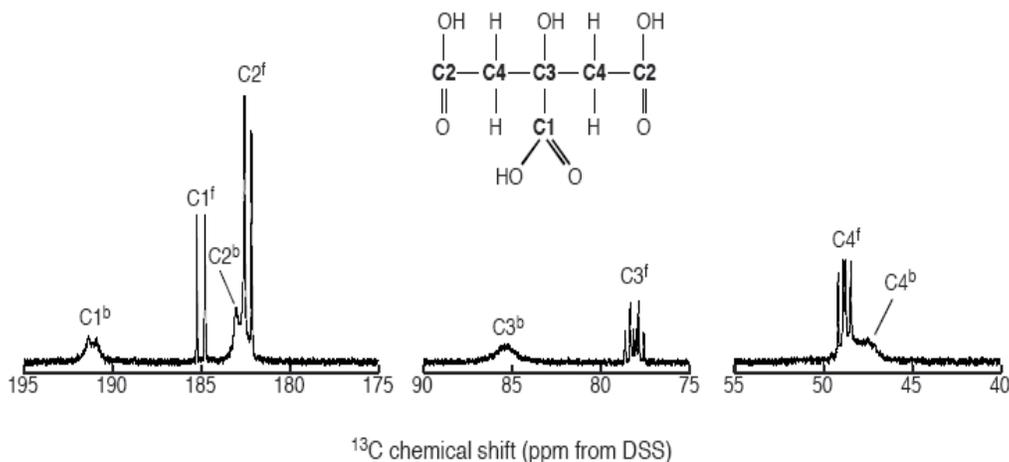


Figure 1. Carbon-13 NMR spectrum of a Th-citrate solution ($[\text{Th}(\text{IV})] = 1.92 \text{ mM}$; $[\text{NaNO}_3] = 3.0 \text{ M}$; $\text{pH} 8.756$). The “f” and “b” superscripts on peak labels identify resonances assigned to the free and bound citrate, respectively. The multiplet structures are a result of the homonuclear scalar interactions that are present in the ^{13}C -enriched citrate.

Th(IV) – Gluconate Complexation

Gluconate is another ligand of importance in selected tank supernatants. It is particularly interesting in the case of actinide complexation owing to its well known affinity for metal ions in the tetravalent state, especially under basic conditions. This fact can be clearly seen in the solubility data on hydrous thorium oxide in the presence of either EDTA or gluconate (Figure 2). EDTA is one of the strongest aqueous chelates known in terms of its ability to solubilize hydrous thorium oxide across a broad range of pH values extending to 11 or 12. However, at higher pH values (typical of HLW tanks) gluconate is an even stronger ligand capable of solubilizing hydrous thorium oxide and by implication other tetravalent actinides.

In FY03 we have obtained the necessary thermodynamic data to evaluate the aqueous Th(IV)-gluconate complexes and to develop an aqueous thermodynamic model. Analysis of this data and manuscript preparation are underway.

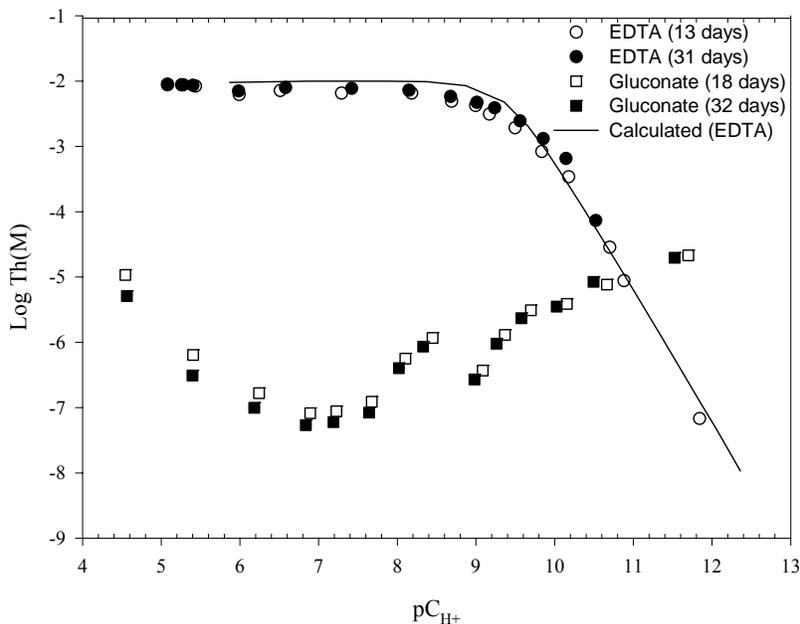


Figure 2. The solubility of hydrous thorium oxide as a function of hydrogen ion concentration (pC_{H^+}) in the presence of either EDTA or gluconate at the same ligand concentration (0.01M).

Ni(II) – EDTA Complexation

In the case of Ni(II) complexation with EDTA we have developed an aqueous thermodynamic model which accurately describes the effects of high base concentration on the complexation of Ni^{2+} by ethylenedinitrilotetraacetic acid (EDTA). The model is primarily developed from an extensive data set on the solubility of $Ni(OH)_2(c)$ in the presence of EDTA and in the presence and absence of Ca^{2+} as the competing metal ion. The solubility data for $Ni(OH)_2(c)$ were obtained in solutions ranging in NaOH concentration from 0.01 to 11.6m, and in Ca^{2+} concentrations extending to saturation with respect to portlandite, $Ca(OH)_2$. The final aqueous thermodynamic model is based upon the equations of Pitzer, accurately predicts the observed solubilities to concentrations as high as 11.6m NaOH (Figure 3) and is consistent with UV-Vis spectroscopic studies of the complexes in solution. These results are in press for publication in the Journal of Solution Chemistry.

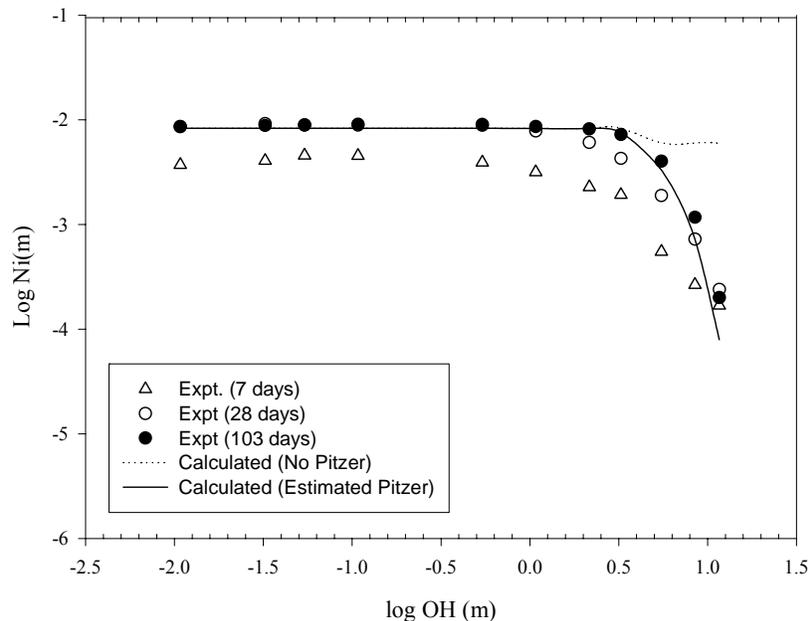


Figure 3. The solubility of $\text{Ni}(\text{OH})_2$ under neutral to basic conditions showing the strong aqueous complexation of $\text{Ni}(\text{II})$ by EDTA which results in solubilizing the stable phase $\text{Ni}(\text{OH})_2$ even to base concentrations as high as 10M NaOH.

Publications

Felmy, A.R., and O. Qafoku. An Aqueous Thermodynamic Model for the Complexation of Nickel with EDTA Valid to High Base Concentration. *Journal of Solution Chemistry* (accepted).

Felmy, A.R., Z. Wang, D.A. Dixon, and N.J. Hess. 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*. (in review)

Felmy A.R., M.J. Mason, O. Qafoku, and D.A. Dixon. Development of Accurate Chemical Equilibrium Models for the Hanford Tanks: The System Na-Ca-Sr-OH- CO_3 - NO_3 -EDT-HEDTA- H_2O . EMSP Symposium Proceedings (in press).

Xia, Y., A.R. Felmy, L. Rao, Z. Wang, N.J. Hess. (2003). "Thermodynamic Model for the Solubility of ThO_2 (am) in the Aqueous Na^+ - H^+ - OH^- - NO_3^- - H_2O - EDTA System." *Radiochimica Acta* 91(12):751-760.

Felmy, A.R., and M.J. Mason. (2003). "An Aqueous Thermodynamic Model for the Complexation of Sodium and Strontium with Organic Chelates valid to High Ionic Strength. I. Ethylenedinitrilotetraacetic acid (EDTA)." *Journal of Solution Chemistry* 32(4):283-300.

Felmy, A.R., M.J. Mason, and O. Qafoku. (2003). "An Aqueous Thermodynamic Model for the Complexation of Sodium and Strontium with Organic Chelators valid to High Ionic Strength. II.

N-(2-hydroxyethyl)ethylenedinitrioltriacetic acid (HEDTA)." Journal of Solution Chemistry 32(4):301-318.

Rustad, J.R., A.R. Felmy, K.M. Rosso, and E.J. Bylaska. (2003). "Ab Initio Investigation of the Structures of NaOH Hydrates and their Na⁺ and OH⁻ Coordination Polyhedra." American Mineralogist 88(2-3):436-449.

Other Contributions

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

We also prepared another version of the “Felmy” database for use by site engineers using the Environmental Simulation (ESP) model.