

Development of Fundamental Data on Chemical Speciation and Solubility for Strontium and Americium in High- Level Waste: Predictive Modeling of Phase Partitioning During Tank Processing

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Principal Investigator

Andrew R. Felmy
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-96
Richland, WA 99352
(509) 376-4079 (phone)
(509) 376-3650 (fax)
ar.felmy@pnl.gov

Co-Investigators

Gregory Choppin
The Florida State University
Department of Chemistry, B-164
Tallahassee, FL 32306-3006
(904) 644-3875 (phone)
(904) 644-8281 (fax)
Choppin@chemmail.chem.fsu.edu

David A. Dixon
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K1-83
Richland, WA 99352
(509) 376-4999 (phone)
(509) 375-6631 (fax)
da.dixon@pnl.gov

Research Objective

In this research program, Pacific Northwest National Laboratory and Florida State University are investigating the speciation of Sr and Am/Cm in the presence of selected organic chelating agents (ethylenediaminetetraacetic acid [EDTA], N-(2-hydroxyethyl)ethylenediaminetriacetic acid [HEDTA], nitrilotriacetic acid [NTA], iminodiacetic acid [IDA], citrate, and oxalate) over ranges of hydroxide, carbonate, ionic strength, and competing metal ion concentrations present in high-level waste stored in tanks at Hanford and other U.S. Department of Energy (DOE) sites.

The project comprises integrated research tasks that approach the problem of chemical speciation using macroscopic thermodynamic measurements of metal-ligand competition reactions, molecular modeling studies to identify structures or complexes of unusual stability, and mass spectrometry measurements of complex charge/mass ratio that can be applied to mixed metal-chelate systems. This fundamental information then is used to develop thermodynamic models designed to predict changes in chemical speciation and solubility resulting from various tank-processing conditions. In this way we can develop new approaches that address fundamental problems in aqueous speciation and, at the same time, provide useful and practical information needed for tank waste processing.

Problem Statement

Current strategies for reducing the total volume of radioactive tank waste requiring disposal at Hanford and other DOE sites call for the development of methods that can be used to selectively dissolve and remove non-radioactive elements, such as Al, P, and Cr, while retaining or precipitating the radioactive elements, including Sr and the actinide elements, in the tank sludge. This partitioning between solids and precipitates is fundamentally dependent on the chemical speciation of the elements present in the tank processing solutions. Of particular importance is separation of the radioactive and hazardous actinide elements and fission products from the sludge and supernatants, particularly from supernatants containing high concentrations of strong chelating agents that can act to dissolve the actinides and fission products as well as interfere with subsequent metal ion extraction processes. Specifically, the fundamental understanding of chemical speciation reactions gained from these studies will help us identify other potential mechanisms (e.g., competition, displacement, or other reactions) that could be used for removing Sr and Am/Cm from organic chelates present in high-level tank waste.

Research Accomplishments

Beginning in October 1996, we initiated a research program on Sr and trivalent actinide speciation in high-ionic-strength, strongly basic solutions that contained organic chelates and competing metal ions. The chemical speciation and solubility data obtained from the initial studies then were used to develop aqueous thermodynamic models, based upon the Pitzer equations, for describing the chemical behavior of these elements in high ionic strength electrolytes.

Initially, our studies focused on determining the effects of hydrolysis (hydroxide concentration) on the chemical speciation of Sr to high base concentration. Next, we studied the effects of carbonate complexation on Sr extending to high carbonate concentration. These initial studies completed our focus on the major inorganic complexants for Sr and formed the foundation for our subsequent studies of organic chelates.

In our studies of organic chelates, the effects of only one competing metal, Ca, were studied. We also studied the effects of hydrolysis and carbonate complexation on the speciation and solubility of Ca because these factors must be known to develop an understanding of the effects of a competing metal ion.

Following completion of the Sr studies, we began our studies of the trivalent actinides using Eu(III) as the analog. These studies identified the potential importance of mixed metal-chelate-hydroxide complexes in waste tank chemistry applications. Studies of Eu(III) complexation of EDTA and NTA under highly basic conditions were completed. No studies on the effects of competing metal ions on the speciation of the trivalent actinides were conducted.

In FY 00, our studies of the trivalent actinides were expanded to include the use of Cm(III). Cm(III) has a much higher fluorescence than Eu(III), so the studies could be conducted at much lower actinide concentrations ($\sim 10^{-8}$ M), thus avoiding the complications introduced by precipitation reactions.

Studies on Cm Speciation

Studies using Time Resolved Laser Luminescence Spectroscopy were performed on Cm(III) solutions over a range of base concentrations and in the presence of three organic chelates: HEDTA, citrate, and oxalate. All three of these chelating agents can be present in certain tank wastes (currently termed Envelope C wastes) that had received complex concentrate additions in the past. These three chelating agents had not been studied at high base concentrations to any significant degree in the past.

Figure 1 shows initial Time Resolved Laser Luminescence Spectroscopy results for these three chelating agents (0.01 M chelate). As expected, at lower base concentration (0.01 M NaOH), all three chelates are capable of complexing Cm(III). However, as the base concentration increases, the weakest of the three chelates is displaced, and only poorly fluorescent hydroxide complexes remain in solution. However, this is not the case for the citrate and HEDTA complexes, which remain in solution even to high base concentration (7.5 M). The significant shift in the peak maximum indicates changing speciation over this concentration range, which in turn is indicative of different numbers of hydroxides bound to the metal-chelate complexes. The results for citrate are particularly surprising since the single metal-chelate complexes for Cm-citrate are significantly weaker than for the corresponding Cm-HEDTA complexes. These studies currently are being conducted over ranges of metal/ligand ratios and base concentrations to better identify the complexes formed and the thermodynamic characteristics of these species.

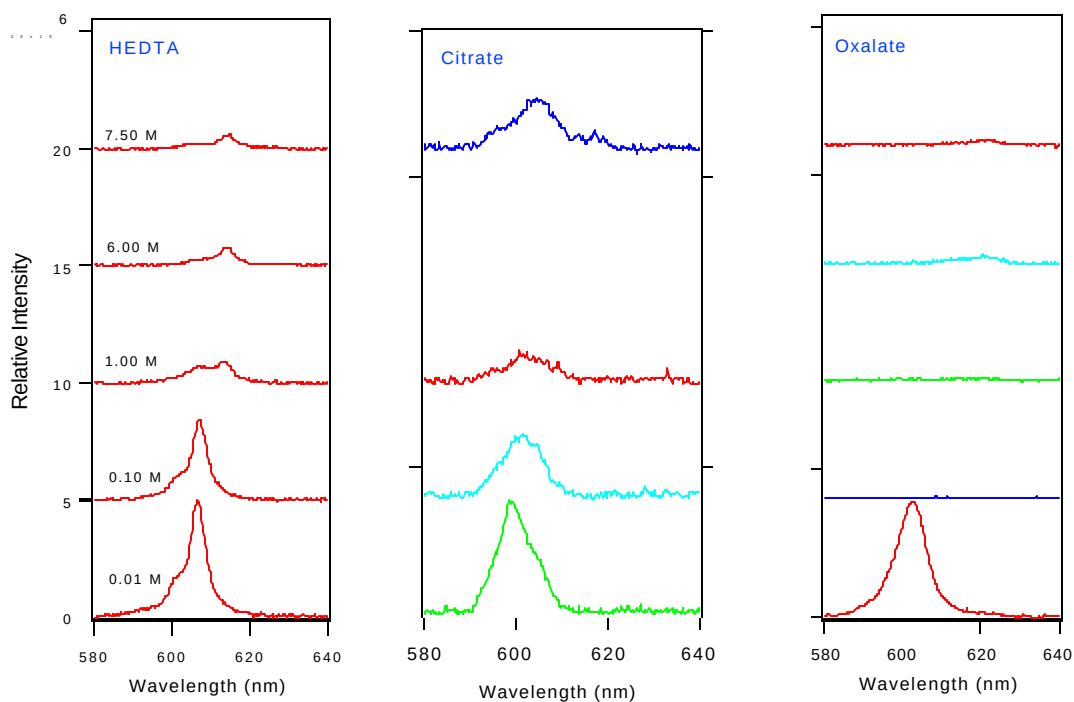


Figure 1. Emission Spectra of Cm(III) Complexes with HEDTA, Citrate, and Oxalate as a Function of NaOH Concentration

Addition of Pitzer's Equations to ESP

During FY01, considerable effort has been spent on incorporating new thermodynamic data (developed under EMSP and elsewhere) into the chemical processing models used at Hanford and other DOE sites. This effort was recognized with a news article in the *CHG Hanford Site News* on the addition of Pitzer's equations to the Environmental Simulation Program (ESP). This enhanced capability will allow all of the new thermodynamic data developed under EMSP to be used by the site contractors.

Planned Activities

In FY02, we plan to finalize our studies of the effects of base concentration on the organic chelates and then initiate studies of mixed metal-chelate-carbonate complexation. Carbonate is present in the Envelope C wastes at high concentrations along with the organic chelates. Although the inorganic speciation reactions of the trivalent actinides with carbonate are known to have high ionic strength, this is not the case in the presence of both carbonate and organic chelates. Like the mixed metal-chelate-hydroxide complexes, carbonate can attach to the central metal in the presence of the chelate because of the asymmetric charge (dipole moment) distribution about the metal-chelate complex. Studies of the competing metal Ni also will be initiated.

Information Access

Felmy AR, Z Wang, DA Dixon, AG Joly, JR Rustad, and M J Mason. 2001. "The Aqueous Complexation of Eu(III) with Organic Chelates at High Base Concentration: Molecular and Thermodynamic Modeling Results." ACS Symposium Series 778, *Nuclear Site Remediation: The First Accomplishments of the Environmental Management Sciences Program*. Chapter 5, pp. 63-82.

Felmy AR, H Cho, JR Rustad, DA Dixon, and GR Choppin. 2000. "The Aqueous Complexation Reactions of Anionic Silica Species to High Concentration." EMSP Vadose Zone Principal Investigators Workshop, November 28, 2000, Richland Washington.

Felmy AR, H Cho, GR Choppin, DA Dixon, GT MacLean, JR Rustad, Z Wang, and Y Xia. 2001. "Development of Accurate Chemical Models for Tank Waste Applications." Tanks Focus Area Mid-Year Review, March 12-15, 2001, Salt Lake City Utah.

Felmy AR, GT MacLean, and S Sanders. 2001. "Inclusion of Pitzer Activity Coefficient Model in ESP." Tanks Focus Area, Salt Dissolution Workshop, May 1-2, 2001, Richland, Washington.

Felmy AR, GT Maclean, and S Sanders. 2001. "The Addition of Pitzer's Equations to ESP." *CHG Hanford Site News*, May 2001, Richland, Washington.

AR Felmy and K Nagy are organizing the Accomplishments of the Environmental Management Sciences Program at the ACS National Meeting, August 26-31 2001, Chicago, Illinois. Six sessions are planned.