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Project Title: **Chemical Speciation of Strontium, Americium, and Curium in High Level Waste: Predictive Modeling of Phase Partitioning During Tank Processing**

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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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Research Objective

In this research program, Pacific Northwest National Laboratory (PNNL) and Florida State University (FSU) are investigating the speciation of strontium and americium/curium in the presence of selected organic chelating agents (ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl) ‘ethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA), and iminodiacetic acid (IDA)) over ranges of hydroxide, carbonate, ionic strength, and competing metal ion concentrations present in high-level waste tanks. The project is composed of 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 spectometry measurements of complex charge/mass ratio that can be applied to mixed metal-chelate systems. This fundamental information is then used to develop thermodynamic models, which allow the prediction of changes in chemical speciation and solubility that can occur in response to changes in 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 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 to selectively dissolve and remove nonradioactive elements such as aluminum, phosphorus, and chromium while retaining or precipitating the radioactive elements, including strontium and the actinide elements, in the tank sludges. This partitioning between solids and precipitates is fundamentally dependent upon 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 sludges and supernatants, particularly from supernatants containing high concentrations of strong chelating agents, which can act to solubilize 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 is needed to propose methodologies for removal of strontium and americium/curium from organic chelates present in high-level tank waste, via competition, displacement or other reactions, without the need for the development of costly and potentially hazardous organic destruction technologies.

Research Progress and Implications

The following section gives a brief description of the progress to date of the PNNL studies. The research at FSU, which is currently focused on the speciation of curium and americium under similar hydroxide and carbonate conditions, will be reported by Professor Choppin in a separate report. This section summarizes the research progress in three main areas: strontium speciation, trivalent actinide speciation, and supporting studies. The supporting studies are focused on solution calorimetry, isopiestic measurements, and applications of capillary electrophoresis-mass spectrometry.

Studies on Strontium Speciation

To unravel the speciation reactions of strontium in complex tank waste requires studies of speciation reactions in the presence and absence of chelators. Specifically, speciation reactions in four chemical systems—Na-Sr-OH-H_2O, Na-Sr-CO_3-H_2O, Na- Ca-OH-H_2O, Na-Ca-CO_3-H_2O, and the mixed system Na-Sr-Ca-OH-CO_3-H_2O with and without added chelators—were studied. The systems including californium as well as strontium were studied to begin to address the issue of metal ion competition and displacement of strontium from the chelates. Californium was chosen for these initial studies because it is present in large amounts in tanks waste; Ca^{2+} has approximately two orders of magnitude higher affinity for the organic chelators than Sr^{2+}.

These studies were largely completed in FY 1998, and the results have been published in the open literature and presented at national society meetings and conferences (Felmy and Mason 1998; Felmy et al. 1998; Felmy et al. 1997a,b,c). These studies resulted in the identification of the species present in these solutions and the development of the necessary thermodynamic data to predict the species' concentrations. The implications of these findings are described below.

Implications of Strontium Studies

The results for strontium have some interesting implications as regards processing basic/ carbonate solutions such as those in high-level tank waste. First, given the expected range in chelate concentrations present in tank waste and the fact that carbonate is present in significant concentration in all tanks, it is likely that the chemical speciation of strontium will be almost certainly unaffected by the presence of IDA and probably also unaffected by the NTA as well. Only HEDTA and EDTA appear to be present at high enough concentrations and to form strong enough complexes to significantly impact the speciation of strontium in tank waste. Such results are important in limiting the number of chemical species that need to be considered in chemical modeling of tank processing strategies. In addition, competition with other metal ions present in such solutions, in this case californium, can effectively displace strontium from the strong chelating agents HEDTA and EDTA, depending upon the concentration of strontium and the competing metal ions. This result indicates that metal ion displacement represents an acceptable alternative to costly and hazardous organic destruction technologies in reducing the impacts of organic chelates in tank processing, especially given the fact that the chelators represent only a small fraction of the total organic carbon in tank waste.

Trivalent Actinide Studies

Considerable progress has also been made in the study of the effects of hydrolysis on the displacement of trivalent actinides and actinide analogs from the organic chelates: EDTA, HEDTA, NTA, and IDA. Studies on the solubility of europium (a trivalent actinide analog) compounds [i.e., $Eu(OH)_3(c)$] have been completed as a function of base concentration in the presence of four organic chelates: EDTA, HEDTA, NTA, and IDA. $Eu(OH)_3(c)$ was chosen for study because of its very low solubility under high base concentration. These studies have shown that high base concentration can displace Eu(III) from all of the organic chelates studied. The effective NaOH concentration for the displacement reaction is dependent on the nature of the specific chelate studied and the chelate concentration.

As an example, the solubility data for $Eu(OH)_3(c)$ in the presence of different concentrations of EDTA (Figure 1) show that at NaOH concentrations >3 M all of the Eu(III) is removed from EDTA solutions (e.g., [EDTA] • 0.01 M). At higher base concentration, the solubility of $Eu(OH)_3(c)$ increases, but this is as a result of the formation of soluble hydrolysis species (e.g., $Eu(OH)_4^-$, ...), not metal-chelate complexes. Similar results have been found for the other chelates (see Figures 2 and 3 for HEDTA and NTA, respectively). These data are also being used to develop accurate

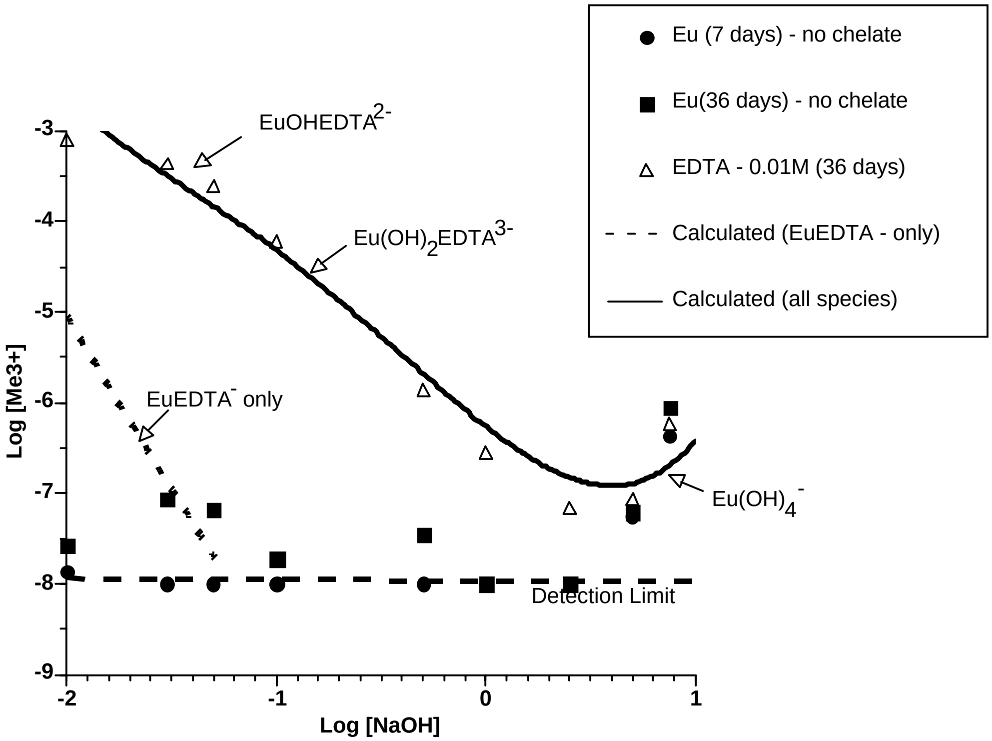

Figure 1. Solubility of $Eu(OH)_3(c)$ in NaOH in the Presence and Absence of Added EDTA

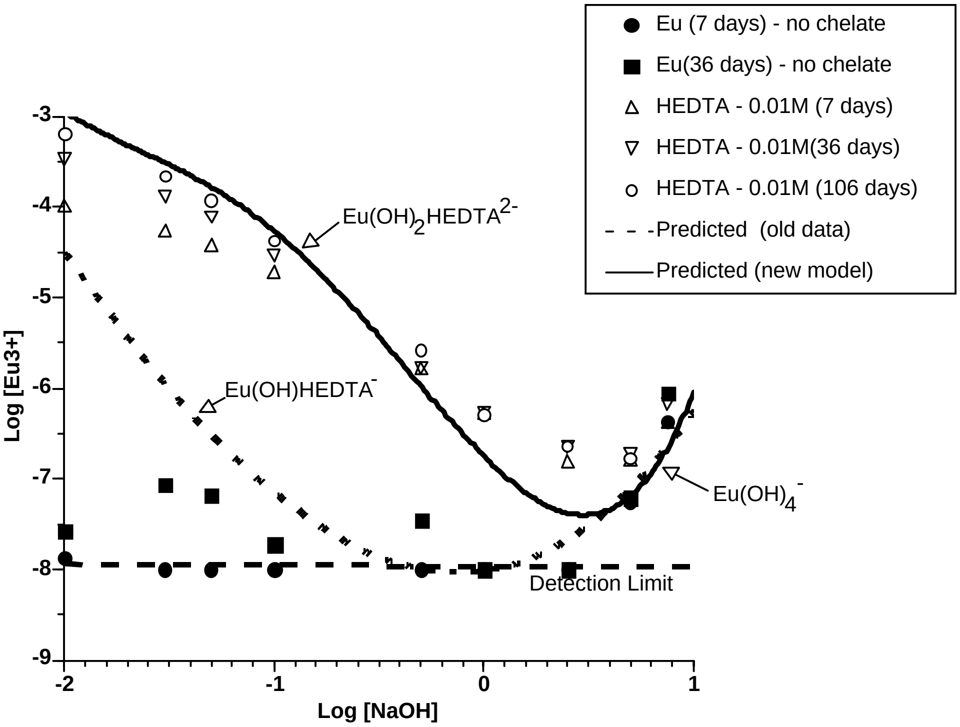

Figure 2. Solubility of $Eu(OH)_3(c)$ in NaOH in the Presence and Absence of Added HEDTA

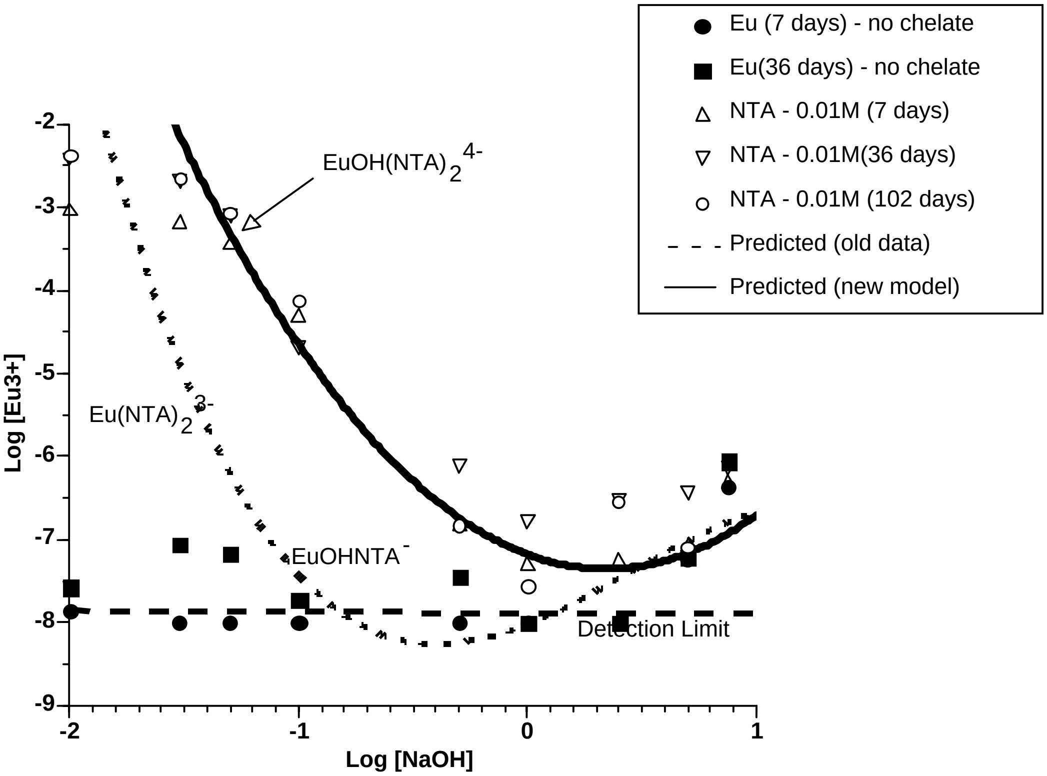

Figure 3. Solubility of $Eu(OH)_3(c)$ in NaOH in the Presence and Absence of Added NTA

thermodynamic models for trivalent actinide species under high base conditions. Such data are important because current thermodynamic models to predict actinide speciation and solubility in these chemical systems underpredict the solubilities by two to four orders of magnitude. As an example of this effect, the model calculations using literature data for the only aqueous complex previously proposed, i.e., $EuEDTA^-$, are several orders of magnitude lower than the experimental results. By using a combination of thermodynamic measurements, molecular modeling simulations, and measurements of fluorescence life times, it is apparent that this discrepancy is the result of the neglect of mixed metal-hydroxide-chelate complexes that form in these highly basic solutions. Using all of these combined data, we have developed a chemical equilibrium model that accurately represents all of the experimental measurements in this chemical system (see Figures 1–3). The calculated stability constants also correlate well with the gas phase binding energies developed from the molecular simulations. These results have been presented at society meetings (Felmy et al. 1999; Felmy and Mason 1998) and in the manuscripts that are in preparation or have been submitted (Felmy et al. 1999; Felmy and Rai 1999).

These models are currently being used by the Hanford private contractor, British Nuclear Fuels, Ltd., in the development of processing strategies for selected tank wastes.

Supporting Studies

In addition to the extensive experimental and computational modeling studies performed under the strontium and trivalent actinide studies outlined above, significant progress has also been made in the areas of solution-phase calorimetry, mass spectrometry, and isopiestic measurements. All three of these areas of study directly enhance our studies of solution-phase speciation.

Solution Phase Calorimetry

Calorimetric measurements are used both to extend the temperature range of validity of our thermodynamic models and to provide useful information on solution-phase reaction kinetics. Studies of reaction kinetics are possible because the heat of reaction is a sensitive parameter that can be directly studied as a function of time. This information is not only useful for developing temperature-dependent thermodynamics models for the organic chelate reactions but also provides useful kinetic information on the exchange of potentially kinetically inhibited species.

Enthalpy of dilution measurements have been conducted on Na_4EDTA-$NaOH$-H_2O mixtures to allow the activity coefficient expressions to be extrapolated over the range of temperatures (25–100°C) needed to develop tank waste processing strategies.

Isopiestic Measurements

Isopiestic studies of electrolyte solutions is a well-established technique for obtaining direct information on the activity of water, which, in turn, through the use of the Gibbs-Duhem relation yields direct information of the solution-phase activity coefficients of the species involved. The method is particularly useful at high electrolyte concentrations such as those relevant to this research. Therefore, as part of this study, extensive isopiestic measurements have been made of osmotic coefficients in the mixed $NaOH$-Na_4EDTA systems. These data are being used to develop better thermodynamic models (i.e., Pitzer ion-interaction coefficients) for Na^+-$EDTA^{4-}$ and OH^--$EDTA^{4-}$ interactions.

The results of the calorimetric and isopiestic measurements have also been presented and published in a number of sources (Oakes et al. 1999; Sterner et al. 1998, 1997a,b; Oakes and Felmy 1998, 1997).

Mass Spectrometry

As part of this study, solution speciation reactions are also planned using capillary electrophoresis-mass spectrometry (CE-MS). CE-MS offers the potential of determining the mass/charge ratio of complexes that may be present in mixed metal-chelate systems where unraveling complex spectral signatures will be difficult or impossible. Our initial results with CE-MS have proven to be effective in identifying metal-EDTA complexes in negative ion mode from mixed electrolyte solutions. This represents the first known combination of CE separation with mass spectrometry detection of metal-organic complexes under negative ion conditions that we are aware of. These results have been presented (Peterson et al. 1998).

Planned Activities

Studies at PNNL have been largely completed and published on the competitive effects of hydrolysis and carbonate complexation of strontium with the organic chelates at 25°C. This effort has resulted in several journal articles and scientific presentations (see below). Studies have also been largely completed with trivalent actinide analogs [using $Eu(OH)_3(c)$] in the presence of high base concentration. Manuscripts have either been submitted or are in preparation. Significant progress has also been made in the areas of solution calorimetry, mass spectrometry, and isopiestic studies. Plans for FY 1999 call for completing and publishing the results to date.

Support for studies in outer years will be required to 1) extend the trivalent actinide model to higher temperatures (>25°C), 2) unravel the speciation of tetravalent actinides (especially Pu(IV)), and 3) include other important competing metal ions, such as nickel, manganese, and lead in the thermodynamic models. Such research is needed, important, and is being used at the Hanford Site.

Publications and Presentations

Felmy AR, DA Dixon, and MJ Mason. 1999. “The aqueous complexation of Eu(III) with organic chelating agents at high base concentration: Correlation of thermodynamic and molecular models.” *J. Solution Chem.* (in preparation).

Felmy AR and D Rai. 1999. “Application of Pitzer’s equations for modeling the aqueous thermodynamics of actinide species: A review.” Invited paper for the special memorial edition of the *Journal of Solution Chemistry* in honor of Professor Kenneth Pitzer (in press).

Felmy AR and MJ Mason. 1998. “The displacement of strontium from organic chelates by hydroxide, carbonate, and calcium in concentrated electrolytes.” *J. Solution Chemistry*, 27(5)435-454.

Felmy AR, DA Dixon, JR Rustad, MJ Mason, and LM Onishi. 1998. "The hydrolysis and carbonate complexation of strontium and calcium in aqueous electrolytes: Use of molecular modeling calculations in the development of aqueous thermodynamic models." *J. Chem. Thermodynamics* 30, 1103-1120.

Oakes CS, SM Sterner, and AR Felmy. 1999. "Thermodynamic properties of aqueous calcium nitrate [$Ca(NO_3)_2$] to 373K including new enthalpy of dilution data." *J. Chem. Thermodynamics* (in press).

Sterner SM, AR Felmy, CS Oakes, and KS Pitzer. 1998. "Correlation of thermodynamic data for aqueous electrolyte solutions to very high ionic strength using INSIGHT: Vapor saturated water activity in the system $CaCl_2$-H_2O to 250°C and solid saturation." *International Journal of Thermophysics*, 19(3)761-770.

Abstracts and Presentations

Felmy AR, DA Dixon, and MJ Mason. March 21-25, 1999. "Aqueous complexation of Eu(III) with organic chelating agents at high base concentration: Molecular and thermodynamic modeling results." 217th ACS National Meeting, Anaheim California.

Felmy AR and MJ Mason. August 9-14, 1998. "The aqueous complexation of Eu(III) with organic chelating agents at high base and high ionic strengths: Metal-chelate displacement induced by hydrolysis and precipitation reactions." 53rd Calorimetry Conference, Midland, Michigan.

Felmy AR, GR Choppin, DA Dixon, and JA Campbell. July 27-30, 1998. "Chemical speciation of strontium, americium, and curium in high-level waste: Predictive modeling of phase partitioning during tank processing." Two presentations and one poster. Presentations to the Hanford Tanks Site Technology Coordination Group (STCG) on November 10, 1998, and to PNNL staff on January 21, 1998. Poster presentation at the EMSP Principal Investigators Workshop, Chicago.

Felmy AR, DA Dixon, JA Campbell, and MJ Mason. September 7-11, 1997a. "The effects of OH, CO_3, and Ca on the displacement of strontium from organic chelates: Implications for waste processing." 214th ACS National Meeting, Las Vegas.

Felmy AR, DA Dixon, and MJ Mason. August 3-8, 1997b. "The complexation of alkaline earth cations by organic chelates at high ionic strength: Competitive effects of hydrolysis and carbonate complextion." 52nd Calorimetry Conference, Asilomar, California.

Felmy AR, DA Dixon, JR Rustad, MJ Mason, and LM Onishi. August 3-8, 1997c. "The use of molecular modeling calculations to improve the development of thermodynamic models: Hydrolysis, carbonate, and EDTA complexation of alkaline earth cations." 52nd Calorimetry Conference, Asilomar, California.

Oakes CS and AR Felmy. August 9-14, 1998. "Thermodynamics of [Na_4EDTA+NaOH]{aq}, including new isopiestic and enthalpy of dilution measurements." 53rd Calorimetry Conference, Midland, Michigan.

Oakes CS and AR Felmy. August 3-8, 1997. "Thermodynamics of [Na_4EDTA+NaOH]{aq}, including new isopiestic measurements, to 373K, 0.1MPa, and stoichiometric ionic strengths of $18{\cdot}9\,mol{\cdot}kg^{-1}$." 52nd Calorimetry Conference, Asilomar, California.

Petersen CE, JA Campbell, AR Felmy, KL Wahl, and JW Finch. May 31-June 4, 1998. “Analysis of metal-organic complexes using CE/MS.” 46th American Society of Mass Spectrometry Meeting, Orlando, Florida.

Sterner SM, AR Felmy, and KS Pitzer. June 22-27, 1997a. “Correlation of thermodynamic data for aqueous electrolyte solutions to very high ionic strength using INSIGHT: Vapor saturated water activity in the system $CaCl_2$-H_2O to 250°C and solid saturation.” Thirteenth Symposium on Thermophysical Properties, Boulder, Colorado.

Sterner SM, AR Felmy, CS Oakes, JM Simonson, and K Pitzer. August 3-8, 1997b. “Thermodynamics of aqueous $CaCl_2$ to 250°C, 400 bars and solid saturation.” 52nd Calorimetry Conference, Asilomar, California.