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

Pacific Northwest National Laboratory
June 1, 1997

Progress Report

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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 Sr and Am/Cm 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, and ionic strength conditions present in high-level waste tanks. This fundamental understanding of chemical speciation reactions is essential to develop methodologies for removal of Sr and Am/Cm from the chelates, via competition, displacement or other reactions, without the need for the development of costly and potentially hazardous organic destruction technologies. These studies specifically focus on the effects of hydrolysis, carbonate concentration, ionic strength, and selected cation competition on the removal of Sr and Am/Cm from the organic chelates.

Research Statement

On a project and scientific basis the project is divided into research tasks: chemical speciation studies, development of molecular models for solution complexes, and development of thermodynamic data and models. This information on chemical speciation is used, in conjunction with certain necessary thermodynamic measurements, to develop thermodynamic models that will 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 simultaneously develop new approaches that address fundamental problems in aqueous speciation and provide useful and practical information needed for tank processing. All of these studies are designed to address key scientific issues involved in chemical speciation studies.

- Current analytical methods for examining the speciation of actinide elements in simple solutions, such as UV-VIS, Raman, etc., develop difficulties in interpreting or analyzing spectral features when multiple complexes are present and contribute to the observed spectra. In this project we are developing molecular models to analyze spectral features and analytical methods, principally based upon mass spectrometry, capable of identifying species present in mixed metal-ligand systems.
- The solubility of several alkaline earth and trivalent actinide compounds under high base conditions is too low for direct chemical speciation measurements. Determining the aqueous speciation in such solutions is currently done largely by curve-fitting solubility data to hypothesized speciation schemes. In this project we are developing molecular-based models to better constrain the possible solution species considered.
- Activity coefficients for aqueous species can change by orders of magnitude in going from dilute solution to the concentrated solutions typical of tank supernatants. Such changes in activity coefficients can dramatically affect the solubility of Sr and trivalent actinide

compounds. In this project we are utilizing the equations of Pitzer to develop such highly accurate models.

The following section gives a brief description on the progress to date of the PNNL studies. The research at FSU, which is currently focused on the speciation of Cu under similar hydroxide and carbonate conditions, will be reported by Professor Choppin in a separate report. The final section summarizes the major accomplishments.

Research Progress

In fiscal year 1997 (FY97) studies at PNNL have been focused on the competitive effects of hydrolysis and carbonate complexation of Sr with the organic chelates. Only initial experiments have been performed with trivalent actinide analogs. Plans call for completing the major portions of the work on Sr in FY97 with the work on the trivalent actinides beginning in FY97 and extending into FY98 and FY99.

Chemical Speciation Studies

Extensive experimental studies have already been conducted on the chemical speciation and solubility of Sr in high base and high carbonate conditions. These studies are summarized as follows.

- Completion of the studies on the hydrolysis and carbonate complexation of Sr and selected alkaline earth cations under high base and high carbonate conditions. These studies have not only identified new chemical species, such as the strong $\text{Sr}(\text{CO}_3)_2^{2-}$ complex at high carbonate concentration, but have also found consistent trends in the stability of alkaline earth hydrolysis and carbonate complexes as predicted from both thermodynamic and molecular models. A manuscript on the results of this research is currently in preparation (see below).
- Completion of the studies on the competitive effects of hydrolysis and carbonate complexation on the displacement of Sr from the EDTA chelate. Interestingly, high base concentration (up to 5M) resulted in little displacement of Sr from the EDTA chelate, owing to the relatively weak hydrolysis of Sr relative to other alkaline earth cations such as Mg^{2+} , but Sr was displaced by high carbonate concentration. An abstract on these results has been accepted for presentation at the next ACS National Meeting, see below, preparation of a manuscript will begin this FY.
- Research on the effects of hydrolysis and carbonate complexation on the displacement of HEDTA, NTA, and IDA have also been initiated. Though not complete, sufficient data are available to contrast the stability of the different chelates at high base and carbonate conditions to allow the submittal of an abstract on these results (see below); the effects of other competing cations, specifically Ca^{2+} , will also be addressed in this presentation.

Progress has also been made on the development of analytical methods capable of determining chemical speciation in complex mixed metal-ligand systems, principally using mass spectrometry (e.g., matrix-assisted laser desorption ionization/time-of-flight mass spectrometry (MALDI/TOF) and electrospray ionization mass spectrometry (ESI-MS). Matrix-assisted laser desorption ionization (MALDI) was designed to provide a simple method for introducing high molecular weight species directly into the gas phase in both neutral and ionic form. Electrospray ionization, a relatively new ionization technique for mass spectrometry, is an effective method for analyzing nonvolatile analytes in solution by mass spectrometry without prior sample alteration (e.g., derivatization). One major advantage of the ESI-MS is that it is a sufficiently gentle ionization technique that noncovalent, weak associations present in solution can be transferred to into the gas phase. The gentleness of the ESI process allows for the preservation of solution associations such as metal-chelator complexes and weak noncovalent associations during the ionization process. Several EDTA solutions under basic conditions have been examined and complexes identified utilizing these methods, including relatively weakly bound sodium ions with the EDTA chelate (i.e., $(\text{EDTA} + 2\text{Na})^{2-}$ at m/z 167)). High concentrations of salt have a tendency to suppress the ion signal. Additional efforts are currently underway using ion exchange to reduce the salt contribution and increase the ion signal.

Molecular Modeling Studies

The initial molecular modeling studies of the Sr-OH, and Sr-CO₃ system have also been completed. Specifically, *ab initio* electronic structure calculations at the density functional theory level with at least a polarized double zeta basis set have been performed. Calculations on the carbonate complexes of Ca²⁺ and Sr²⁺ have been completed for 1,2, and 3 carbonate groups. Calculations on Ca²⁺(H₂O)₆, Ca²⁺(H₂O)₅, and Ca⁺(H₂O)₅(OH) have also been done. One interesting aspect of these results is that although the proton binding energies for the hydrated Ca and Sr complexes are similar and correlate well with our speciation and thermodynamic measurements, the molecular modeling results indicate quite different microscopic explanations for the observed hydrolysis behavior. The calculations show that the acidity of Ca²⁺(H₂O)₆ is 168 kcal/mol at the nonlocal DFT level and that extensive hydrogen bonding of the H₂O molecules to the OH⁻ in the isolated complex occurs. The structure of Sr⁺(H₂O)₇(OH) shows a completely different structure with the OH dissociating from the complex and hydrogen bonded only to three complexed H₂O molecules. The acidity of the octavalent Sr complex is 166 kcal/mol. The nmr chemical shifts for the Ca and Sr complexes have also been calculated. These studies provide unique insight into possible chemical speciation effects, especially in solutions where it was not possible to experimentally determine the speciation directly. These results are currently being summarized in a paper being prepared for the Journal of Solution Chemistry (see below).

The structures of NTA, IDA, and EDTA and different anions of these acids have also been optimized and vibrational spectra calculated. These results will be used to calculate the various acidities of the complexing agents. An important result is the need to treat hydrogen bonding between the acids and the carboxylate groups in these species. We will complete the above calculations and optimize complexes of Sr⁺² with EDTA and the other complexing agents during the remaining part of the FY.

Thermodynamic Modeling Studies

Early this FY a preliminary thermodynamic model was developed, based upon the equations of Pitzer, to describe the changes in chemical speciation and solubility of Sr that can occur in tank processing solutions with changes in base concentration, carbonate complexation, and EDTA concentration. The specific chemical system addressed was the Na-Ca-Mg-Sr-OH-CO₃-EDTA-NO₃-H₂O system at 25°C. This model was developed as an initial guide to help design specific experimental studies on chemical speciation and was based upon the extensive amount of experimental data in the literature on EDTA complexation. Unfortunately, although an extensive amount of reliable experimental data are available to parameterize the model at low ionic strength and low base concentration (i.e., <0.1m NaOH), this did not prove to be the case at higher ionic strength and high base concentration. As a result, the predictions of this initial model did not prove to be quantitatively accurate when compared to the new experimental data obtained in this study at high ionic strength. The key model deficiency proved to be the interactions of the bulk cations and anions (i.e., Na⁺, NO₃⁻, OH⁻...) with the highly charged EDTA⁴⁻ species, which dominates at pH values greater than 12. The necessary thermodynamic measurements, specifically osmotic coefficient measurements, are currently being conducted to obtain the necessary data to improve the accuracy of the model. Although delays in opening the new Environmental and Molecular Sciences Laboratory has hampered progress on these measurements, sufficient data have been obtained to submit an abstract on the EDTA⁴⁻-NaOH system (see below). In addition, a small effort was initiated to upgrade an existing chemical equilibrium model to better incorporate all of the thermodynamic data available for the organic chelates and develop thermodynamically consistent equations of state. An abstract on this effort has also been prepared (see below).

Summary of Accomplishments

- The studies on the hydrolysis and carbonate complexation of Sr and selected alkaline earth cations under high base and high carbonate conditions has been completed. A manuscript is being prepared.
- The studies on the competitive effects of hydrolysis and carbonate complexation on the displacement of Sr from the EDTA chelate has been completed. An abstract has been submitted.
- An abstract has been submitted on research progress on the displacement reactions of Sr and Ca complexes with HEDTA, NTA, and IDA at high ionic strengths.
- Molecular modeling studies on alkaline earth cations hydrolysis and carbonate complexation has been completed. Studies on organic chelate structure and complexation has been initiated.
- An initial thermodynamic model for the Na-Ca-Mg-Sr-OH-CO₂-EDTA-NO₃-H₂O system at 25°C has been completed. Experimental studies to develop key needed parameters have also been initiated.

- A meeting has taken place with the Co-PI, Professor Choppin, in February to discuss progress on the project and coordination of research efforts.

Papers and Abstracts

Felmy, A.R., D.A. Dixon, J.A. Campbell, and M.J. Mason. 1997. "The Effects of OH, CO₂, and Ca on the Displacement of Sr from the EDTA Chelate: Implications for Waste Processing." Abstracted accepted for *the ACS National Meeting*, Las Vegas NV, September 7- 11, 1997.

Felmy, A.R., D.A. Dixon, and M.J. Mason. 1997. "The Complexation of Alkaline Earth Cations by Organic Chelates at High Ionic Strength: Competitive Effects of Hydrolysis and Carbonate Complexation." Abstract accepted for the *52nd Calorimetry Conference*, Asilomar, CA August 4-8, 1997.

Felmy, A.R., D.A. Dixon, and M.J. Mason. "Hydrolysis and Carbonate Complexation of Alkaline Earth Cations: Consistency of Thermodynamic and Molecular Modeling Results." To be submitted to *the Journal of Solution Chemistry*.

Oakes, C.S. and A.R. Felmy, 1997. "Thermodynamics of [Na₄EDTA+NaOH]{aq}, Including New Isopiestic Measurements to 373K." Abstract accepted for *the 52nd Calorimetry Conference*, Asilomar, CA August 4-8, 1997.

Sterner, S.M., A.R. Felmy, J.R. Rustad, and K.S. Pitzer, 1997. "Thermodynamic Analysis of Aqueous Solutions Using 'Insight'." Abstract accepted for the *International Symposium on Hydrothermal Reactions*, Gatlinburg, TN July 22-24, 1997.