

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

## Principal Investigators

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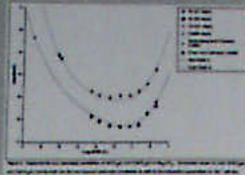
## Objectives

- Determine the effects of hydrolysis, carbonate complexation, and selected metal ion displacement on Sr and trivalent actinide speciation.
- Answer Key Questions:
  - Are the trivalent actinides and fission products complexed (or likely to be complexed) with the chelates? If so, which chelates?
  - Can the hazardous elements be removed from the chelates with relatively simple metal ion displacement reactions or is more difficult and expensive organic destruction required?
  - If displacement is possible, can an effective processing strategy be designed?

## Key Results

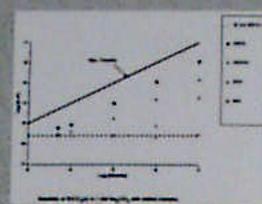
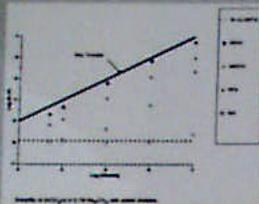
- Chemical Speciation of Sr in high ionic strength solutions containing hydroxide, carbonate, and organic chelators determined.
- Only the strongest chelators in the tank solutions (EDTA, HEDTA) can out compete the inorganic ligands and effect speciation.
- Metal ion displacement reactions can remove Sr from even the strongest chelators.
- Base displacement (via hydrolysis and precipitation) can remove the trivalent actinides from solution even in the presence of high chelate concentrations.
- Overall results indicate that metal ion or base displacement reactions may offer an acceptable alternative to organic destruction in treating complex concentrate waste at the Hanford site.

- $\text{SrCO}_3(\text{c})$  readily precipitates and is insoluble.
- Speciation information can be obtained directly from solubility displacement
- DFT Calculations in gas phase indicate only two carbonates per Sr cation.

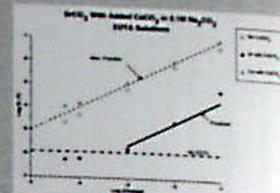
■ Na-Sr-OH-CO<sub>2</sub>-H<sub>2</sub>O

- $\text{Sr}^{2+} + \text{CO}_3^{2-} = \text{SrCO}_3(\text{aq})$  2.81 (lit.)
- $\text{SrCO}_3(\text{aq}) + \text{CO}_2 = \text{Sr}(\text{CO}_3)_2$  0.50
- $\beta^0(\text{Na}^+ \cdot \text{Sr}(\text{CO}_3)_2) = -15$
- Consistent with molecular modeling (2 carbonates)
- Difference between Log K values small (7)

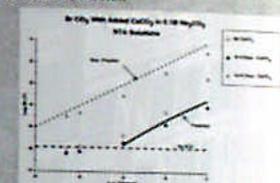
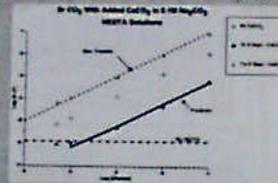
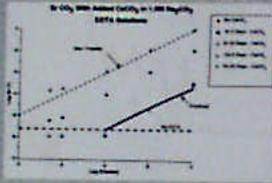
Carbonate can displace chelates at concentrations present in tank wastes except for EDTA, HEDTA



Ca is effective in displacing Sr from even the strongest chelates



Simple predictive relationships, resulting from cancellation of activity coefficient variations, predict cation displacement ( $\text{SrL}_2 + \text{CaCO}_3(\text{c}) = \text{CaL}_2 + \text{SrCO}_3(\text{c})$ ) in concentrated solutions.



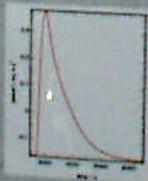
## Supplemental Studies

**Mass Spectrometry** - Speciation in Complex Solutions (ESI-MS and CE-MS) Analysis

**Isopiestic Measurements** - Activity Coefficients for Na<sub>4</sub>EDTA, Na<sub>4</sub>HEDTA, and Na<sub>4</sub>NTA Solutions

**Calorimetry** - information on temperature effects and kinetics

**Example:**  $\text{SrL}_2 + \text{CaCO}_3(\text{c}) = \text{CaL}_2 + \text{SrCO}_3(\text{c})$  heats



## Papers and Abstracts

■ Felmy A.R., and M.J. Mason (1998). The Displacement of Sr from Organic Chelates by Hydroxide, Carbonate and Calcium in Concentrated Electrolytes. *J. Solution Chem.* 27(5), 435-453.

■ Felmy, A.R., D.A. Dixon, J.R. Rustad, M.J. Mason and L.M. Onishi. The Hydrolysis and Carbonate Complexation of Strontium and Calcium in Aqueous Solution: Use of Molecular Modeling Calculations in the Development of Aqueous Thermodynamic Models. Accepted for publication *Journal of Chemical Thermodynamics*.

■ Felmy, A.R., D.A. Dixon, J.R. Rustad, L.M. Onishi, and M.J. Mason. 1997. The Use of Molecular Modeling Calculations to Improve the Development Thermodynamic Models: Hydrolysis, Carbonate, and EDTA Complexation of Alkaline Earth Cations. *52nd Calorimetry Conference*, Asilomar CA, August 3-8, 1997.

■ Oakes C.S., and A.R. Felmy. 1997. Thermodynamics of [Na<sub>4</sub>EDTA+NaOH] (aq) including isopiestic measurements to 373K, 0.1MPa, and stoichiometric ionic strengths of 18.9mol/Kg. *52nd Calorimetry Conference*, Asilomar CA, August 3-8, 1997.

■ Felmy, A.R., D.A. Dixon, J.A. Campbell, M.J. Mason, L.M. Onishi, and J.A. Campbell. 1997. "The Effects of OH, CO<sub>2</sub>, and Ca on the Displacement of Sr from Organic Chelates: Implications for Waste Processing." *214th ACS National Meeting*, Las Vegas NV, September 7-11, 1997.

■ Sterner S.M., A.R. Felmy, and R.S. Pitzer. Correlation of Thermodynamic Data for Aqueous Solutions to Very High Ionic Strengths using INSIGHT: Vapour Saturated Water Activity in the system CaCl<sub>2</sub>-H<sub>2</sub>O to 250°C and Solid Saturation. *Thirteenth Symposium on Thermophysical Properties* (in press).

■ Petersen, C.E., J.A. Campbell, A.R. Felmy, K. L. Wahl, and J.W. Fitch. Analysis of Metal-Organic Complexes Using CE/MS. Presented at the 46th American Society of Mass Spectrometry, Orlando, FL, May 31-June 4, 1998.

■ Felmy, A.R., and M.J. Mason (1998). The Aqueous Complexation of Eu(III) with Organic Chelating Agents at High Base and High Ionic Strengths: Metal Chelate Displacement Induced Hydrolysis and Precipitation Reactions. *53rd Calorimetry Conference*, August 9-15, Midland MI.

## Background

- High Level waste tanks at DOE sites contain
  - fission products (Sr, Tc...)
  - actinides (Am, Cm, ...)
  - high concentrations of OH, NO<sub>3</sub>, CO<sub>3</sub>, ...
  - chelators EDTA, HEDTA, NTA, ...

- Strong inorganic and organic complexes can form.
- Effect processing strategies
  - solubilization of metal ions from sludge
  - efficiency of solvent extraction processes
  - may necessitate removal of organics

- Impact of organic chelates dependent on concentration and presence of other metal ions
  - chelate concentrations can be significant but account for only a small fraction of the total organic carbon
  - several metal ions can react with the chelates

- Studies difficult
  - Complex solutions, high ionic strengths, variable temperatures
  - Speciation difficult to experimentally determine
    - matrix interferences
    - multiple species - complex spectra
    - maybe present at low concentration
  - Thermodynamic modeling - difficult
    - species assumed - "curve fitting"

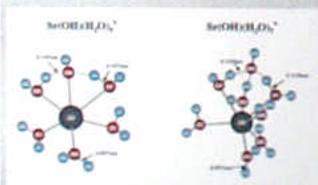
## Approach

- Experimentally determine the effects of ligand-metal competition
  - very limited data sets/thermodynamic models on chelates at high base concentration (>0.1M)
- Determine the speciation in these solutions
  - Utilize new advances in molecular modeling (DFT)
    - defining more appropriate speciation schemes.
    - criteria for use of activity coefficient formulations vs inclusion of complex species.
    - identify key molecular clusters of unusual stability.
  - Experimental methods
    - ESI-MS, MALDI, ... - applicable to multiple species
    - Analysis of Solubility data
    - Curve displacement - speciation

## Results

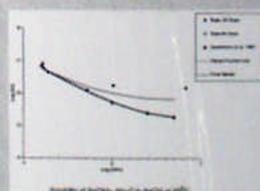
### Hydrolysis

DFT Calculations - indicate no strong association of Sr and Hydroxyl



Structure of gaseous Sr(OH)<sub>2</sub> and Sr(OH)<sub>2</sub>·OH calculated by DFT.

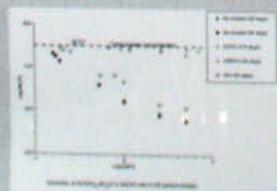
Solubility studies confirm weak association of Sr with hydroxyl even to high base.



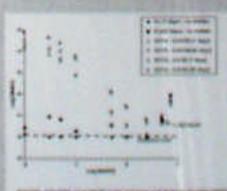
Hydrolysis reactions effective in displacing into the weakest chelates

- Thermodynamics Data Developed
  - Ion-interaction approach appropriate
  - parameters reasonable
    - $\beta^0(\text{Sr}^{2+}\text{-OH}^-) = -.06$
    - $\beta^1(\text{Sr}^{2+}\text{-OH}^-) = 1.65$
    - $\theta(\text{Na}^+\text{-Sr}^{2+}) = \theta(\text{Na}^+\text{-Ca}^{2+}) = -.07$
  - Consistent with molecular models

Solubility of Sr(OH)<sub>2</sub>·8H<sub>2</sub>O in NaOH with 0.1M Added Chelators



High base is effective in displacing trivalent actinides from even the strongest organic chelates.



### Summary of Hydrolysis Effects

- Ion-interaction approach works well for modeling Sr, and there is no evidence for second hydrolysis species.
- Hydrolysis has little impact on displacing Sr from chelates (except possibly IDA) but can be effective in displacing trivalent actinides.
- DFT calculations consistent with solution phase thermodynamics.
- Manuscripts published or in press.