The Chemical Speciation of Sr and Trivalent Actinides in Tank Waste: Implications for subsurface transport and waste processing

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EMSP Workshop, Richland WA, May 6-7 2003

The Pacific Northwest National Laboratory, Richland WA

AN-107 Diluted Feed Composition

(Felmy et al. 2000)

Major Compounds	Concentration (m)	Minor Components	Concentration (m)	Organic Ligands	Concentration (m)
Na^{+}	8.9	Al	1.7×10^{-1}	Glycolate	.30
NO_3^{-}	3.1	Ba	3.4×10^{-5}	Gluconate	.022
NO_2^{-}	1.3	Ca	1.3×10^{-2}	Citrate	.055
CO_3^{2-}	1.6	Ce	2.3×10^{-4}	EDTA	.024
OH^{-}	0.84	Cd	4.9×10^{-4}	HEDTA	.0094
SO_4^{2-}	0.1	Cr	3.3×10^{-3}	NTA	.037
PO_4^{3-}	0.037	Cs	1.1×10^{-4}	IDA	.056
*F^{-}	0.39	Cu	3.9×10^{-4}		
Cl^{-}	0.046	Fe	2.4×10^{-2}		
		K	3.8×10^{-2}		
		La	1.9×10^{-4}		
		Mn	2.3×10^{-3}		
		Nd	5.8×10^{-4}		
		Ni	7.9×10^{-3}		
		Pb	1.45×10^{-3}		
		Sr	3.5×10^{-5}		
		U	3.6×10^{-4}		
		Zn	3.4×10^{-4}		
		Zr	5.6×10^{-4}		

* IC analysis probably includes formate and acetate

Radionuclides

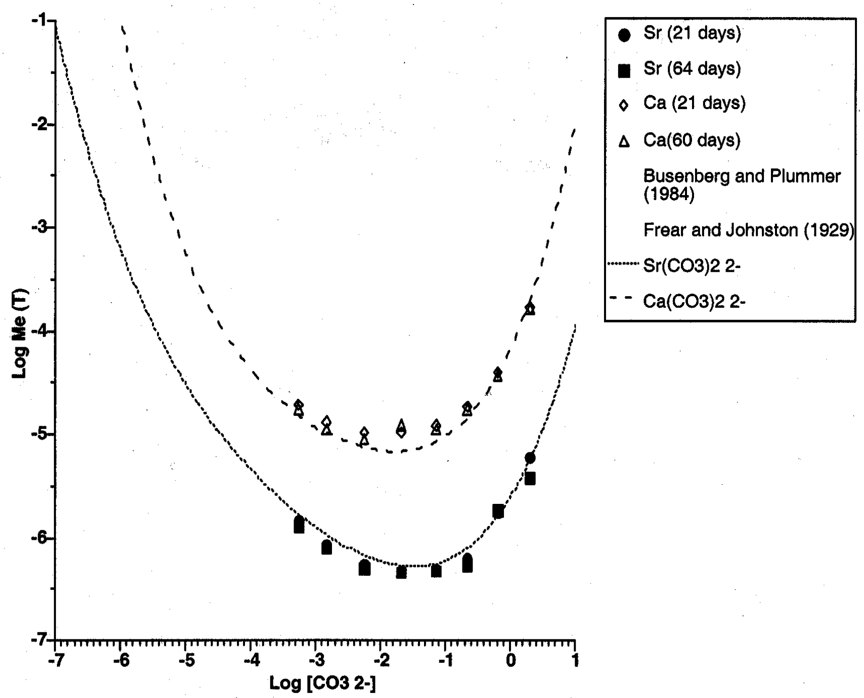
(Tank AN-102, Urie et al. 2002)

Analyte	Supernatant (μCi/ml)	Wet Centrifuged Solids (μCi/g)
^{60}Co	8.49E-02	5.71E-02
^{90}Sr	5.72E+01	1.44E+02
^{99}Tc	1.48E-01	9.88E-02
^{125}Sb	NM	2.E-01
^{137}Cs	3.69E+02	2.16E+02
^{152}Eu	NM	1.E-02
^{154}Eu	2.31E-01	5.12E-01
^{155}Eu	1.00E-01	3.20E-01
^{238}U	NM	2.18E-05
^{237}Np	1.20E-04	9.21E-04
^{238}Pu	1.65E-03	1.19E-02
^{239}Pu	6.47E-03	5.56E-02
^{240}Pu	2.01E-03	1.50E-02
$^{239/240}Pu$	5.90E-03	4.17E-02
^{241}Am	1.65E-01	4.21E-01
^{242}Cm	6.29E-04	2.E-03
$^{243/244}Cm$	6.71E-03	1.72E-02

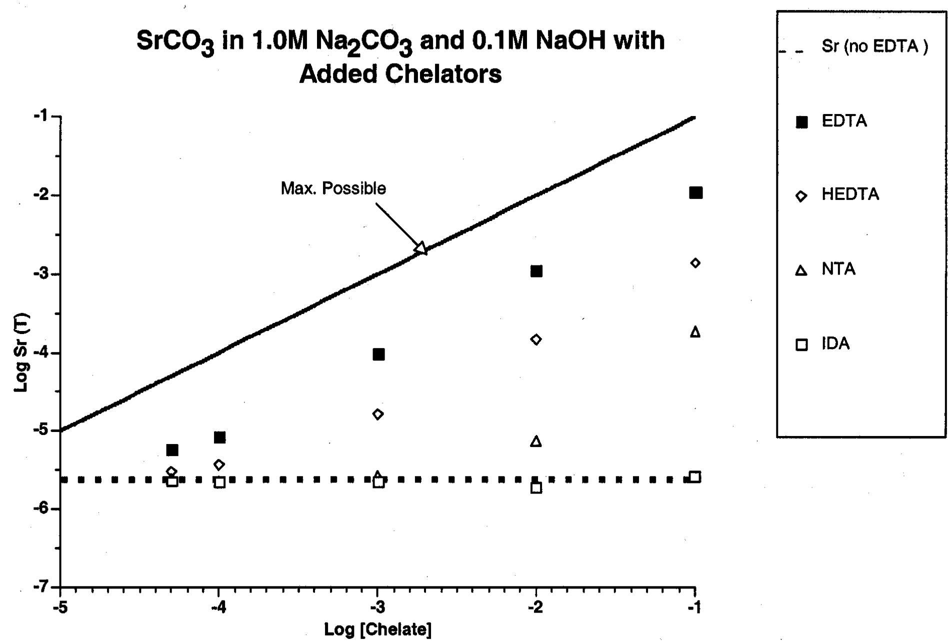
NM – not measured

Sr Speciation

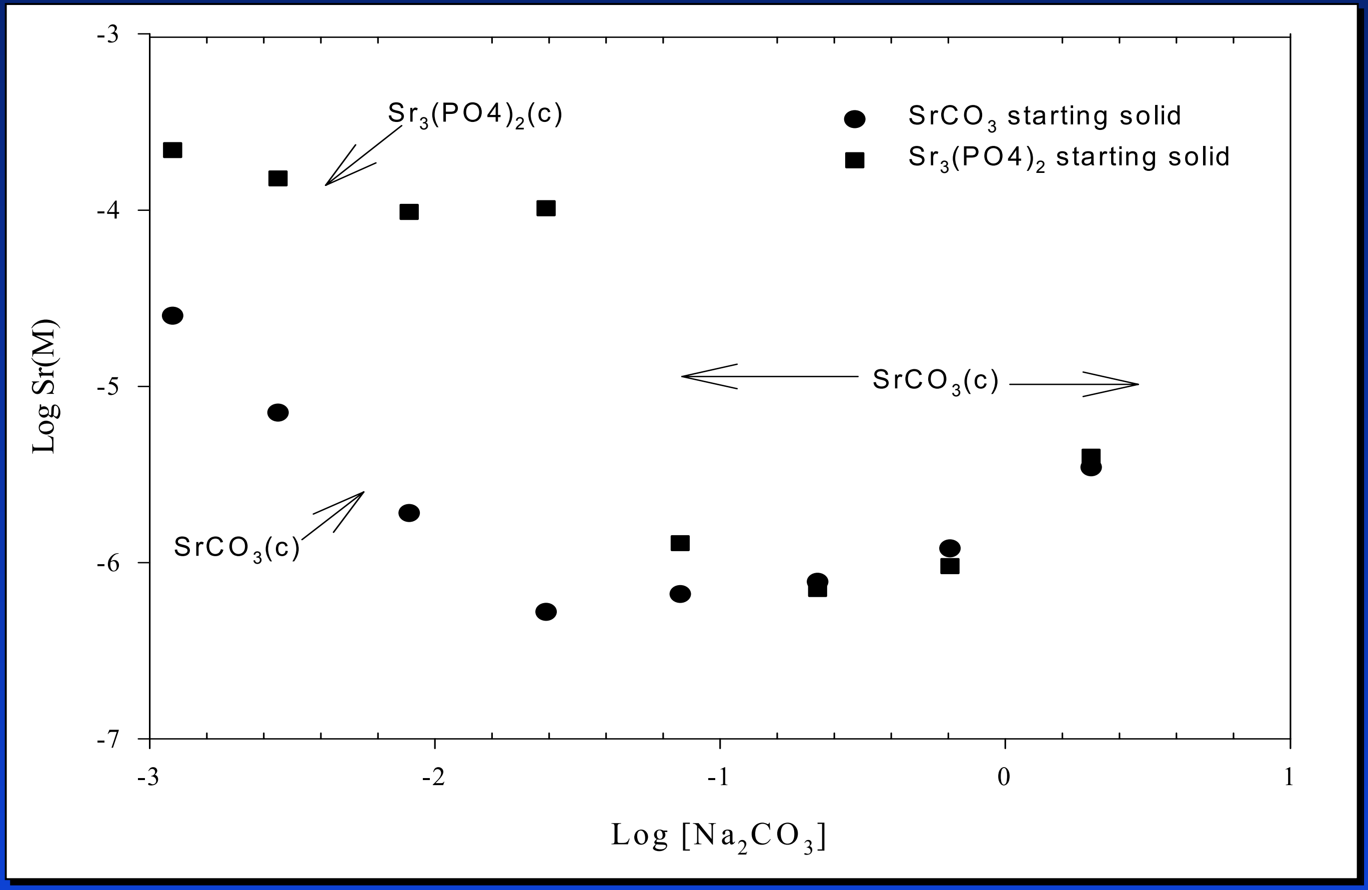
- Developed a thermodynamic model for predicting the aqueous speciation and solubility of Sr in the tank waste.
- Began with inorganic Na-Ca-Sr-OH-CO_3-H_2O system to high ionic strength.
  - Sr^{2+}-OH^- interactions weak
  - Strongest inorganic complexes ($SrCO_3$(aq), $Sr(CO_3)_2^{2-}$)
- Conducted chelate displacement studies as a function of carbonate concentration for several of the possible chelators in tank waste.
  - If the chelate complexes are too weak to displace $Sr(CO_3)_2^{2-}$ then there is no need for definitive data.



Solubility of $SrCO_3$ in Na_2CO_3 showing formation of $Sr(CO_3)_2^{2-}$ (e.g., $SrCO_3(c) + CO_3^{2-} = Sr(CO_3)_2^{2-}$)



The Solubility of $SrCO_3$ in 1.0M Na_2CO_3 with Organic Chelates

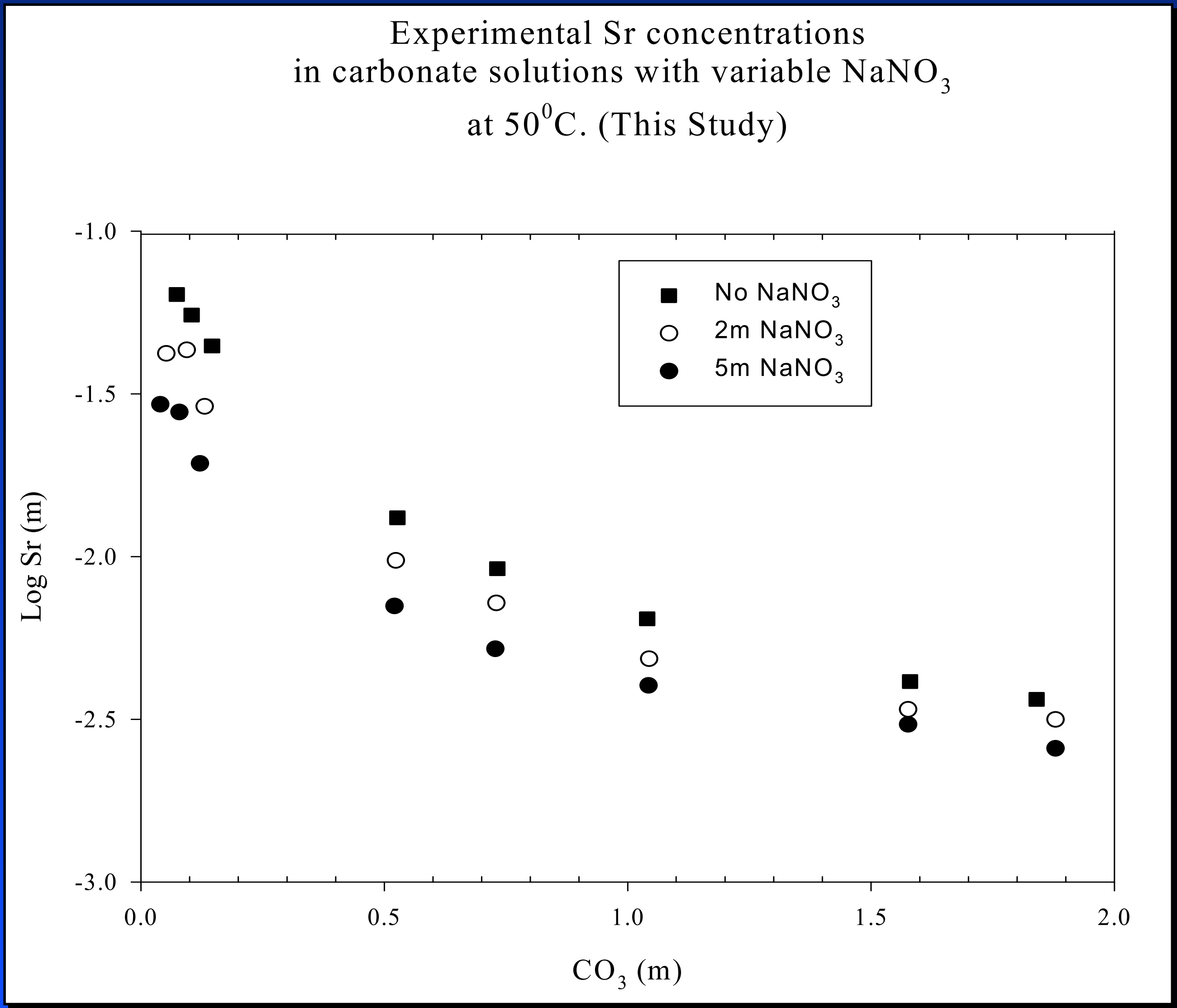


Stability of $SrCO_3$(c) and $Sr_3(PO4)_2$(c) starting materials as a function of added Na_2CO_3.
Initial PO_4 concentration in the $Sr_3(PO4)_2$(c) experiments was 0.03M.
Samples equilibrated for 357 days.

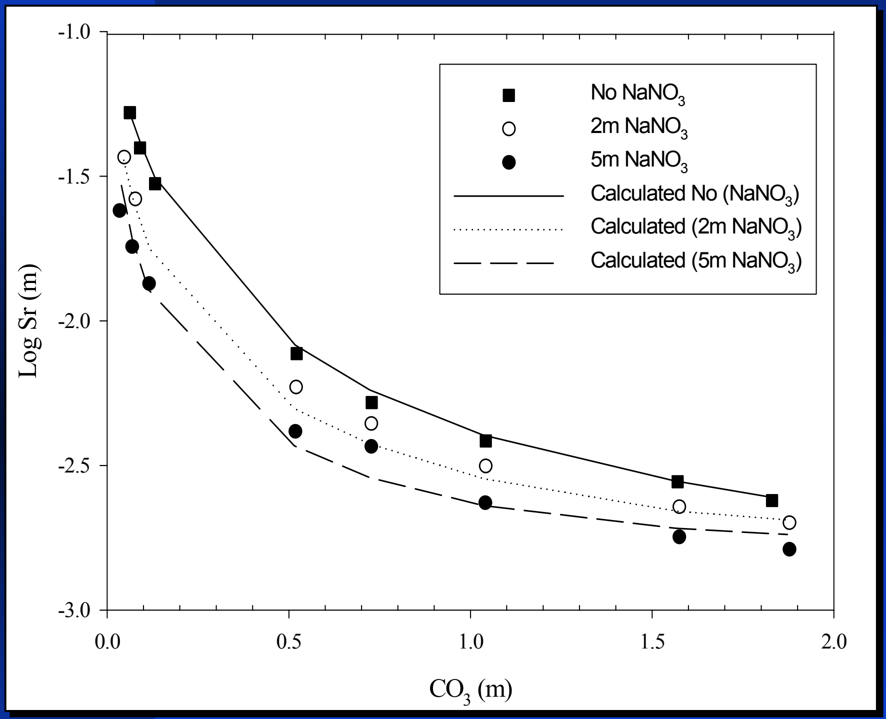
Comprehensive Studies

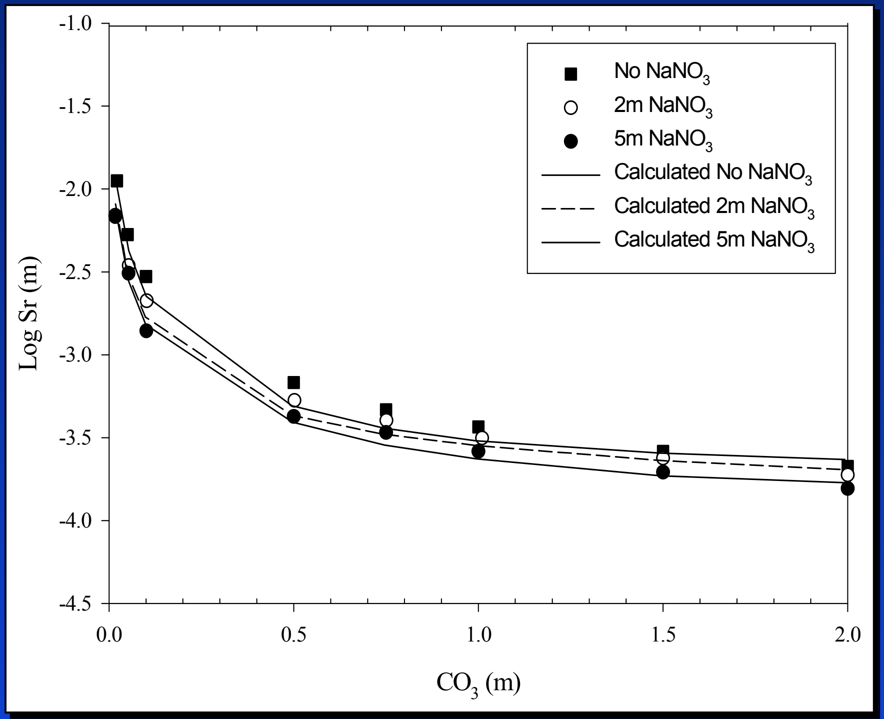
- Developed an **extensive** set of solubility data for $SrCO_3$.
  - Temperatures (25 –75°C)
  - Na_2CO_3 (0.01m to 1.8m)
  - $NaNO_3$ (0 to 5m, extends to 9m total Na)
  - EDTA and HEDTA included
  - Data set should span the range of conditions expected in tank processing.

Effects of Na^+ on $SrEDTA^{2-}$ Stability



Final Thermodynamic Modeling

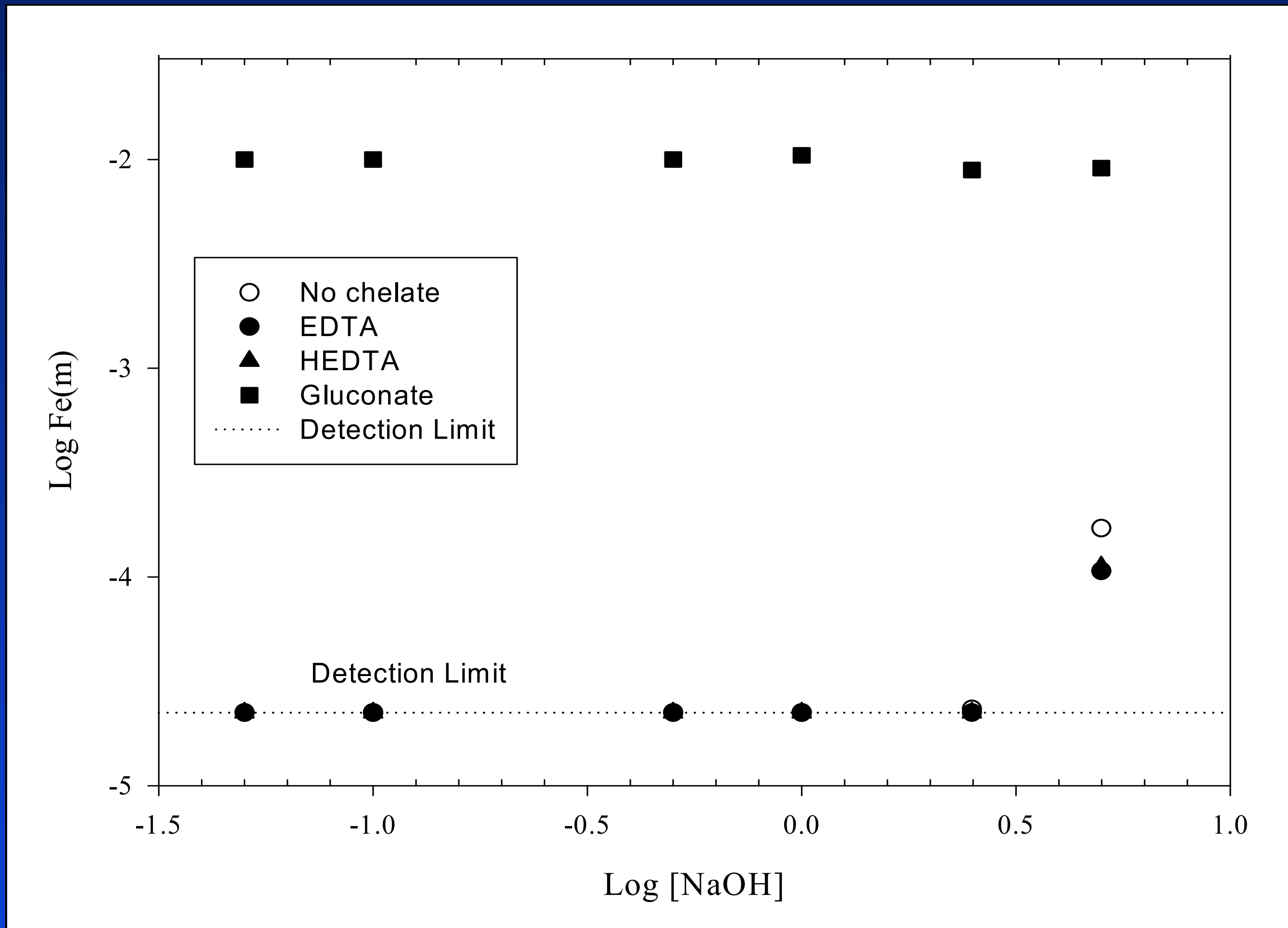




The solubility of $SrCO_3$(c) with added EDTA (a) and HEDTA (b) as a function of carbonate concentration at different concentrations of $NaNO_3$ and a over the temperature of 75°C. 0.1M chelate concentrations.

Competing Metal Ions

- Four metal ions besides Sr are potentially important EDTA or HEDTA.
  - Al, Fe, Ca and Ni
  - Metal ion competition for the chelates can dramatically effect the solubility of $SrCO_3$.
  - Preliminary studies reduced this to only Ca and Ni.
  - The thermodynamics for Na-Ca-OH-CO_3-EDTA-HEDTA-H_2O and Na-Ni-OH-CO_3-EDTA-HEDTA-H_2O systems is also required.

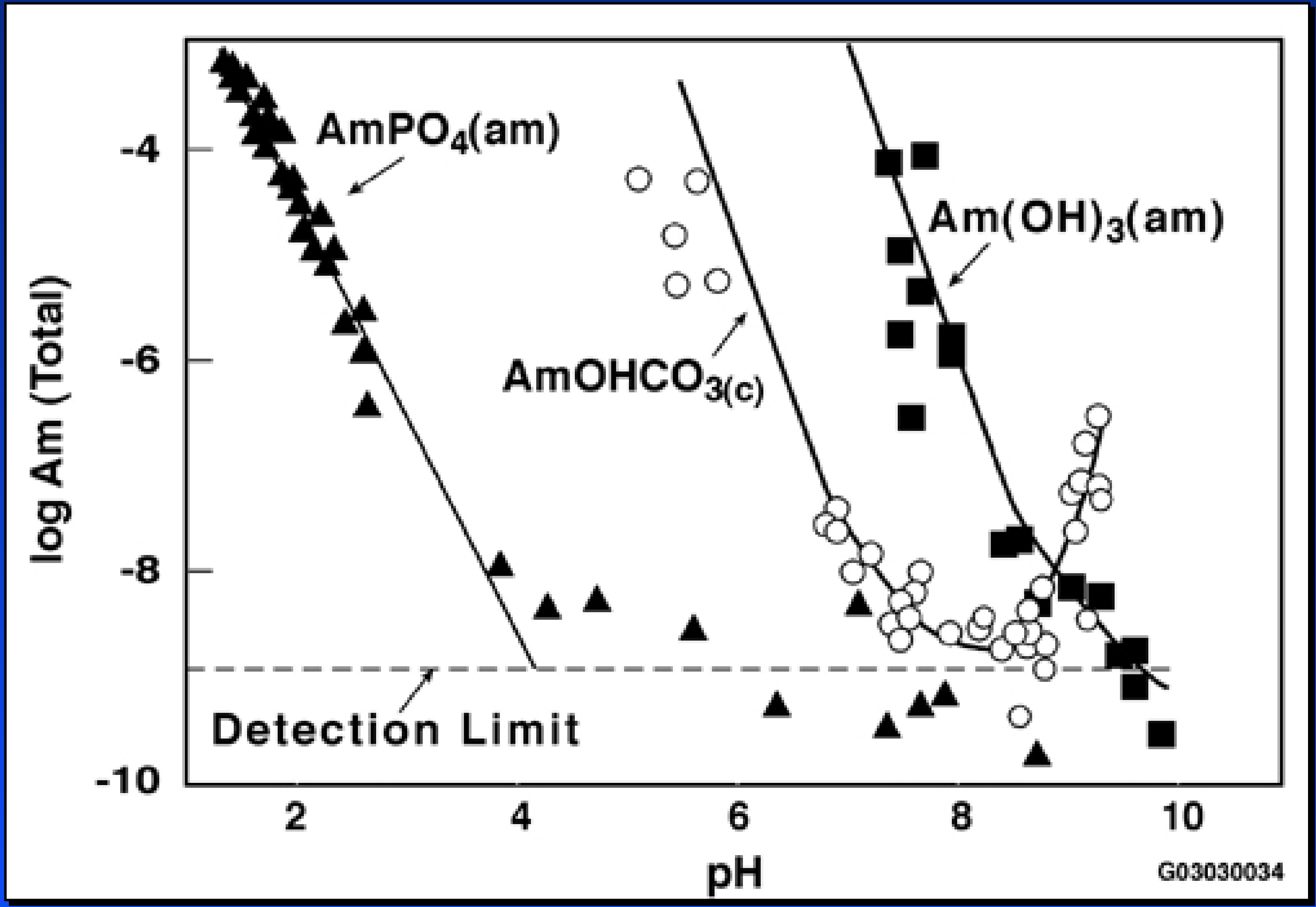


The solubility of $Fe(OH)_3$(am) in the presence and absence of 0.01M EDTA, HEDTA or gluconate as a function of NaOH concentration. Equilibration time 7 days.

Trivalent Actinide Speciation

- Thermodynamic models for inorganic ligands available
  - Includes: OH, SO_4, PO_4, F, CO_3, NO_3 (review of Felmy and Rai 1999)
  - Predict dominant species in the waste tanks should be either carbonates ($An(CO_3)_3^{3-}$ or hydrolysis species ($An(OH)_4^-$) and the stable solid should be the hydroxide
  - Aqueous concentrations low (10^{-8}M)

Trivalent Actinide Phase Boundaries



Approach (focus on chelates)

- Solubility studies on $Eu(OH)_3$ as a function of chelate and base concentration.
  - EDTA, HEDTA, NTA, initiated gluconate
  - Chelate ineffective in solubilizing hydroxide precipitate cannot be a dominant aqueous species.
- Eu(III) and Cm(III) fluorescence measurements of speciation.
- Molecular simulations of species structure and binding energy.

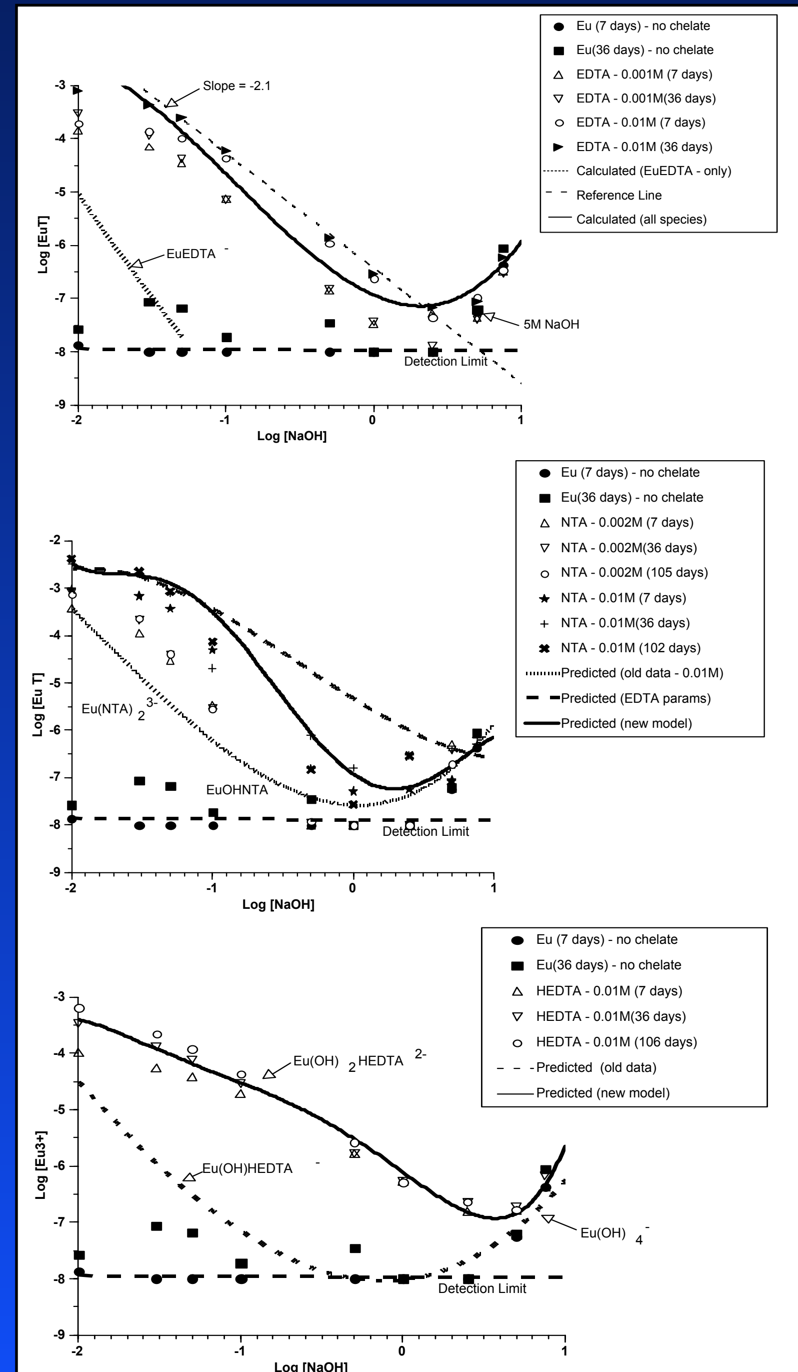
$Eu(OH)_3(c)$ Solubility in the presence of chelators at high base

EDTA

Modeled by assuming the presence of mixed metal-chelate-hydroxide complexes

NTA

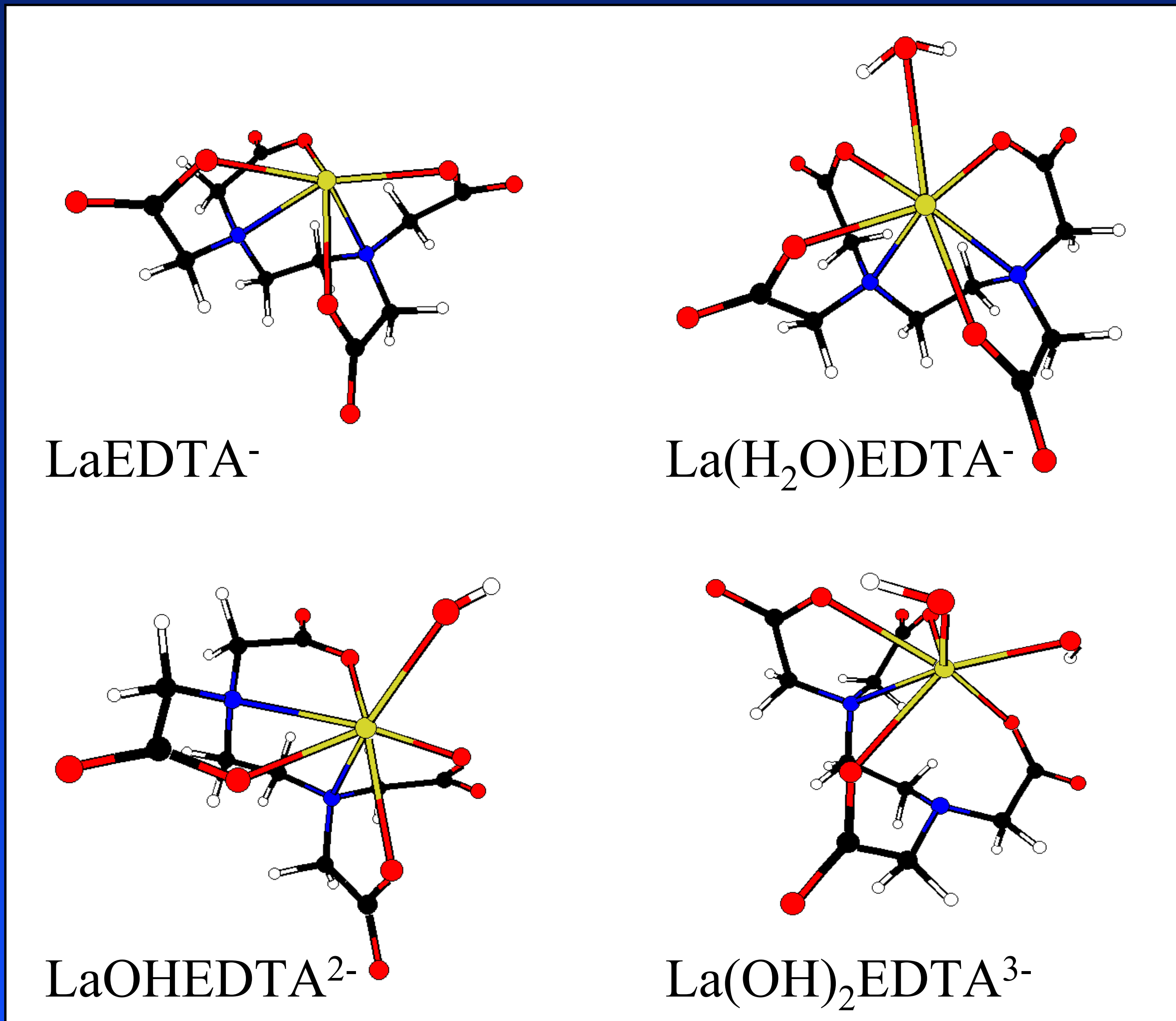
HEDTA



Solubility of $Eu(OH)_3(c)$ in NaOH in the presence and absence of added HEDTA.

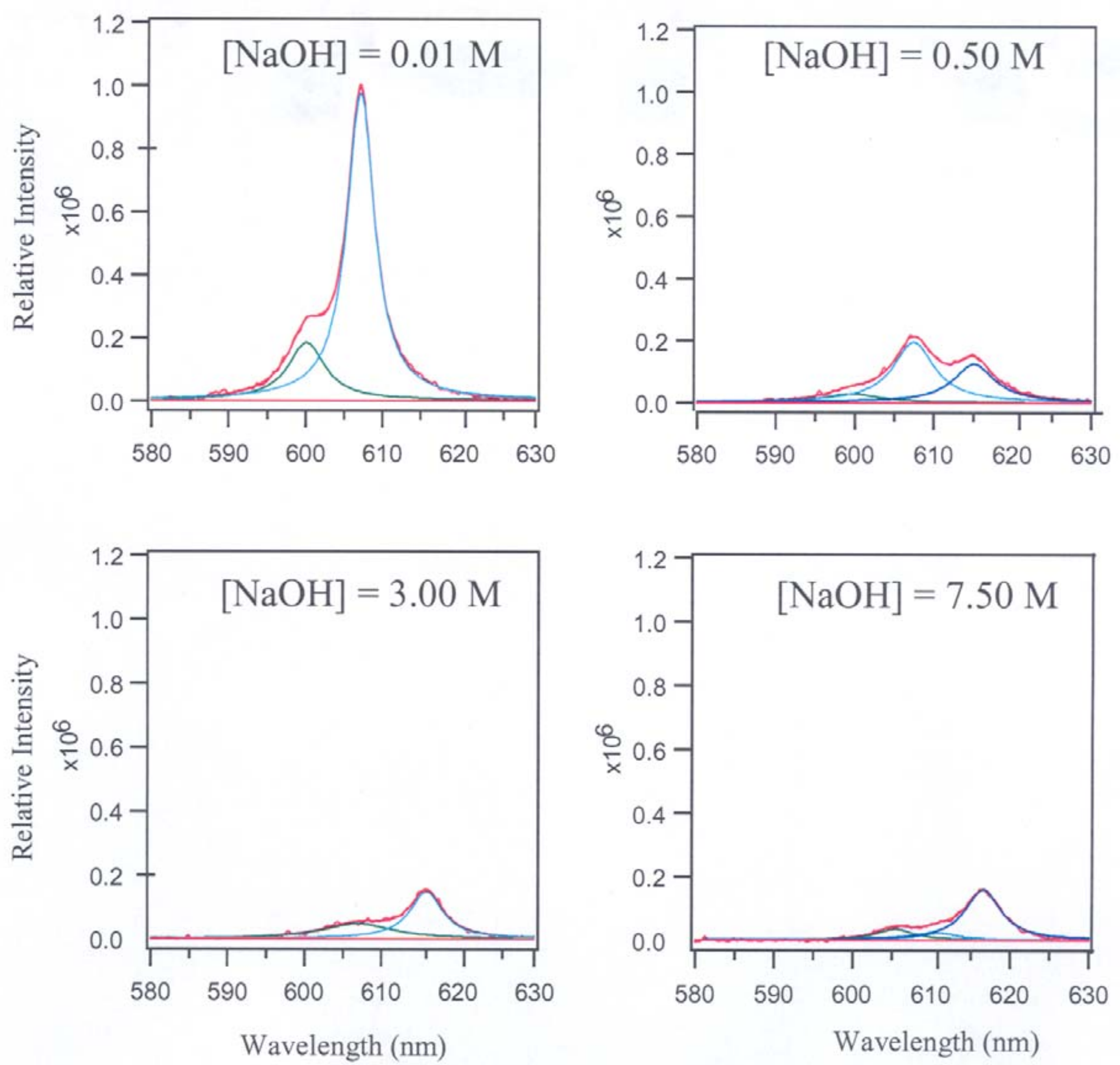
From Felmy et al. (2001)

Asymmetry of Chelate-metal Binding allows Formation of Mixed Metal-chelate-inorganic Species



Fluorescence Emission Spectra of Cm(III) in The Presence of HEDTA at Different NaOH Concentrations

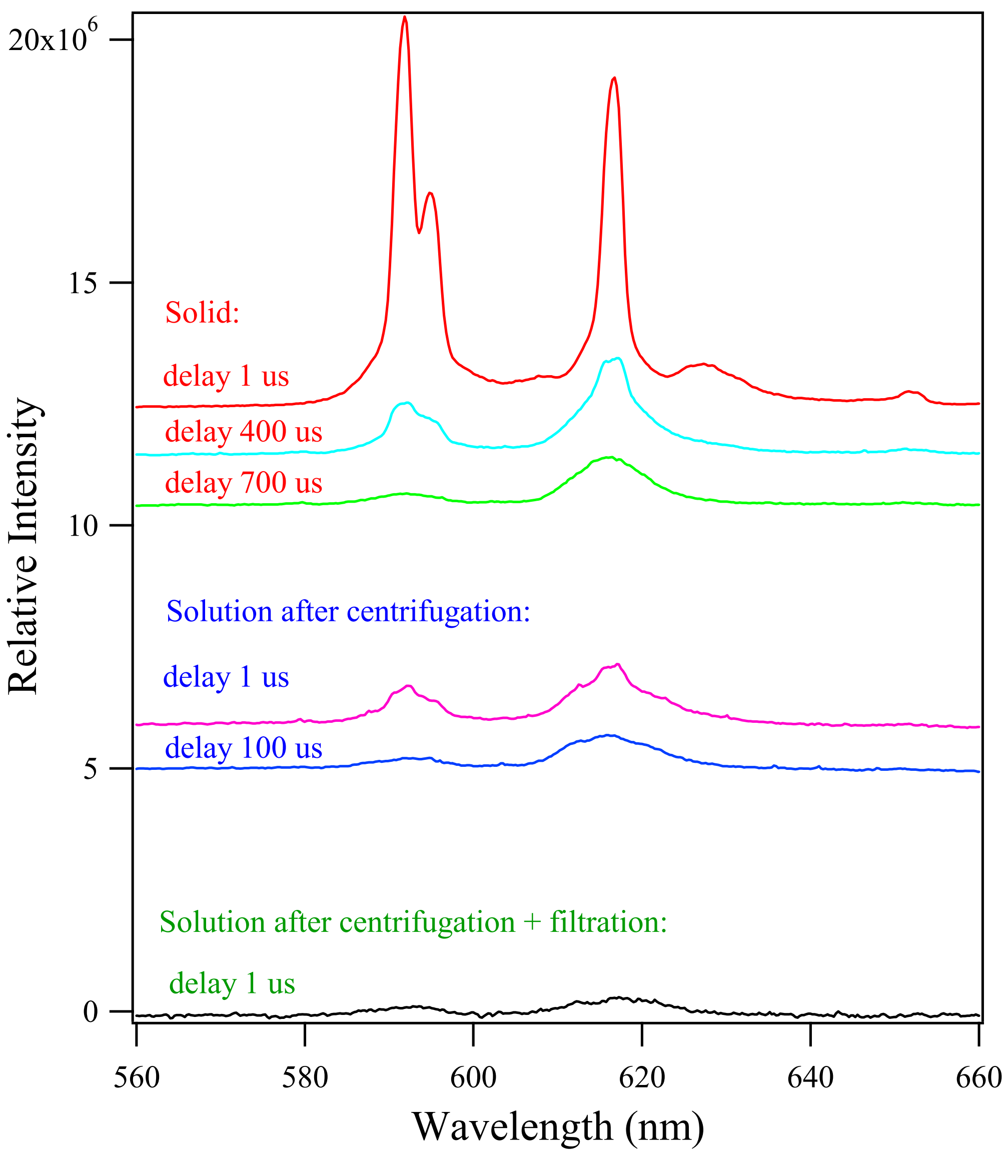
[Cm(III)] = 9.6 x 10^{-9} M; [HEDTA] = 0.01 M; λ_{ex} = 375 nm



- Simulation of fluorescence intensity data for the species with λ_{max} = 617 nm fails to produce a constant stability constant

Time-resolved Fluorescence Emission Spectra of Eu(III) in the Presence of 0.001 M HEDTA and Excess Solid $Eu(OH)_3$ (s)

Reaction time: 72 hours; filter pore size ~ 4 nm; λ_{ex} = 375 nm



- Strong sorption of HEDTA at solid europium hydroxide
- Centrifugation leaves europium hydroxide particulates in the solution
- Further filtration removes most europium oxide particles

Other Studies

- Silicate complexation of Sr, Co, and trivalent actinides
  - Sr – only weakly complexed
  - Trivalent actinides – strong monomeric and polymeric complexes
- Tetravalent actinide – chelate complexation
  - EDTA, citrate, gluconate
    - Gluconate the strongest at high base – may stabilize Am(IV) especially in the presence of permanganate
- Initiated studies on U(VI) speciation at very high carbonate and phosphate (BX – tank waste) – accurate source term

Chemical Speciation in Tank Waste (Current Situation)

- Sr speciation
  - Absence of chelates – dominated by neutral or anionic carbonate complexes
  - Presence of chelates – simple metal-chelate complexes ($SrEDTA^{2-}$)
    - Accurate thermodynamic models available
- Trivalent actinides/analogs (Am, Cm)
  - Low base
    - No chelate – carbonate complexes ($Am(CO_3)_3^{3-}$)
    - Chelates – mixed metal-hydroxyl-chelate complexes
    - Thermodynamic models available (25^0C)
  - High base (0.1 (no chelate) to 0.5M (chelates) NaOH)
    - Nanoparticle release from the tanks could dominate
- Importance of silica speciation (Am, Co), tetravalent actinide complexation (chelates), and U(VI) phosphate/carbonate being studied