The Aqueous Thermodynamics and Complexation Reactions of Radionuclides to High Ionic Strength:

Applications in Subsurface Science and High-Level Waste Processing

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Background

- Virtually all chemical reactions in HLW processing or subsurface science occur in contact with aqueous solutions.
  - Many of these solutions have unique properties in terms of the ionic strength, acid/base characteristics, and components present in solution.
  - Knowledge of the aqueous species present and the thermodynamics of their complexation reactions in complex mixtures impacts.
    - waste pretreatment, tank waste retrieval, analysis of impact of tank residuals, and in determining the migration of radionuclides in the subsurface.

Examples of Different Waste Compositions

- Pretreatment (AN-107 diluted feed)
  - Na (8.9m)
  - OH (0.84m)
  - CO_3 (1.6m)
  - EDTA (0.024m)
  - HEDTA 0.01m)
  - NTA (0.037)
  - Ca (.013m)
  - Ni (0.0079)
- EDTA complexed with Ca and Ni.
- Tank Retrieval (C-106 oxalic acid treatment)
  - Oxalate (1M)
  - Al (0.24M)
  - Fe(0.05M)
  - Mn (0.05M)
  - Na (0.46M)
  - Sr-90 (401 mCi/l)
- Oxalate completely complexed with Al and Fe [$Al(Ox)_3^{3-}$, Fe ($Fe(Ox)_3^{3-}$, …]

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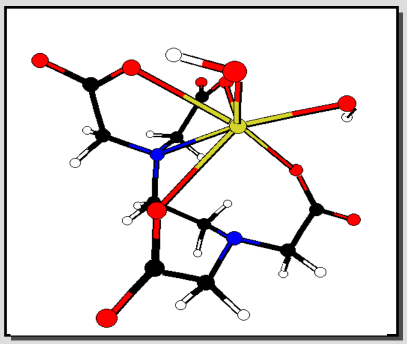
Approach

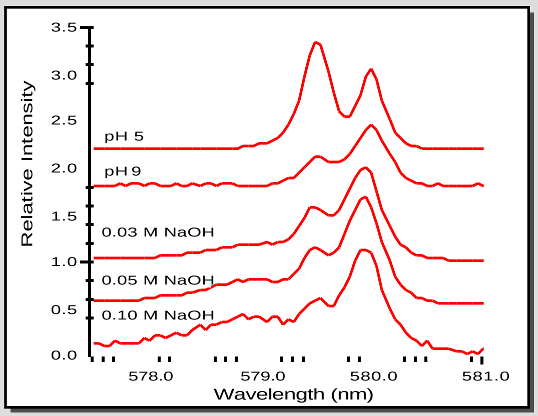
Molecular Simulations
(metal-EDTA-OH Complexes)
-Structures
-Energetics

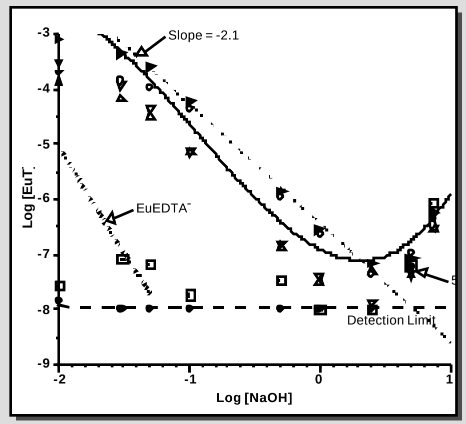
Fluorescence Spectroscopy
(Eu/Cm-EDTA)
-# of species present
-Associated Hydroxyls

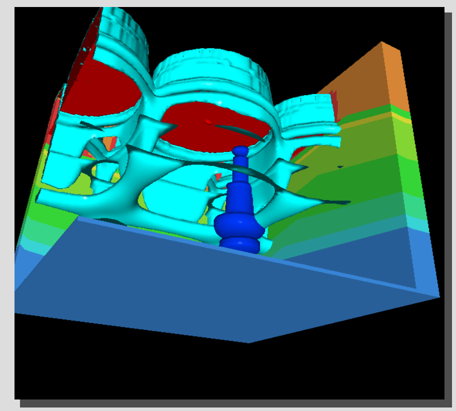
Thermodynamic Data for Complexes

Thermodynamic Models For Subsurface and Waste Tank Applications
(Basic, concentrated solutions)









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Approach

- Evaluate the species present in solution.
  - Combination of experimental techniques (NMR, XAS, TRLFS, IR, …) and molecular simulation.
- Develop accurate thermodynamic models for the key species as a function of electrolyte and base composition.
- Incorporate these data in both reactive transport model and chemical processing models used at Hanford.
- Work with site contractors (Bechtel National, CHG, or their contracted research staff) on model application.

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Current Situation

- Current thermodynamic model development focusing on the subsurface and the impacts of tank residuals on closure.
  - Waste Treatment Plant under construction.
    - R&D programs cut back in the pretreatment area.
  - Workshop scheduled for this spring March 3 and 4 to define key scientific challenges related to the nature of the residuals and their impacts on final tank closure.

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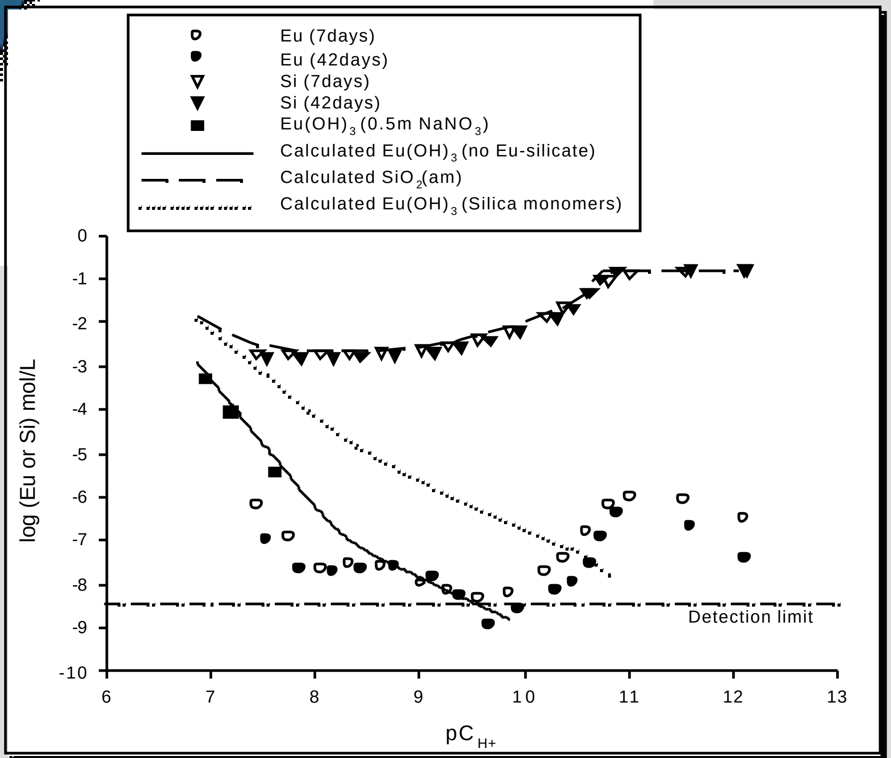
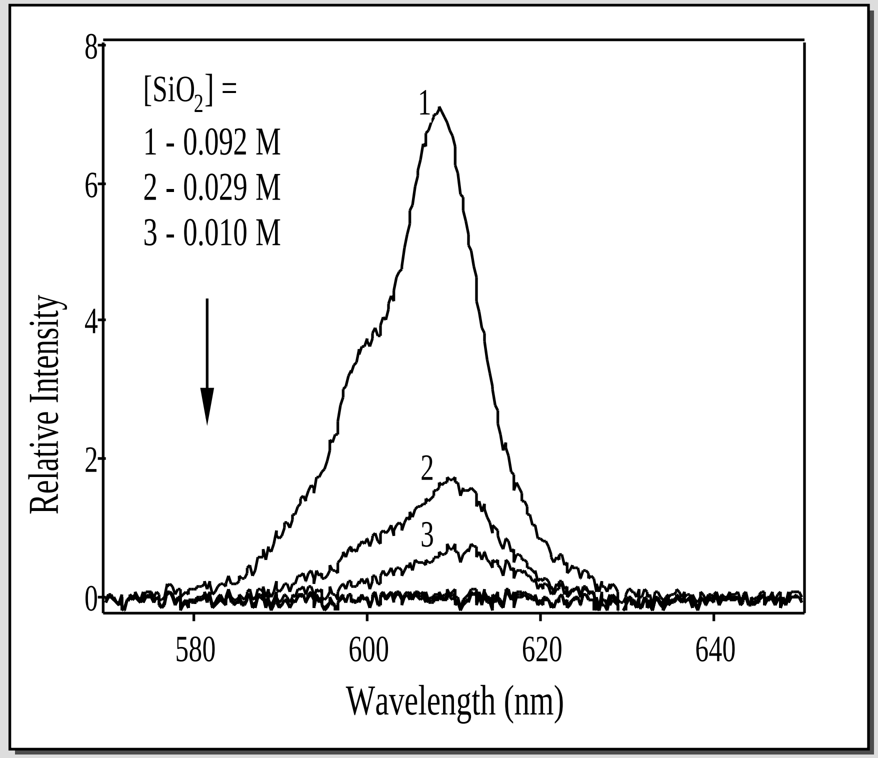
Recent Accomplishments

- Defined the importance of polysilicate complexation of trivalent radionuclides at high base concentration.
- Developed a new thermodynamic model for U(VI)-carbonate species to high concentration.
  - New Ksp's for Cejkaite ($Na_4UO_2(CO_3)_3$) and $NaUO_2PO_4$(c).
  - Cejkaite in C-203 residuals – our data in the release models.
- Demonstrated the importance of nanoparticles in misinterpreting thermodynamic data.
- Analogy between U(VI) and Pu(VI)in phosphate solids.
- Demonstrated the importance of chelate (or chelate-metal complex) adsorption to the solid phase in limiting radionuclide migration.
- Included our thermodynamic model GMIN in the reactive transport models used at Hanford and provided an updated thermodynamic database.
  - Reactive transport models : Lichtner (LANL), Steefel (LBL), and Yabusaki and Onishi (PNNL).

Eu(III)/Cm(III)-Polysilicate Complexation (previously unidentified species)



Increases solubility at high pH

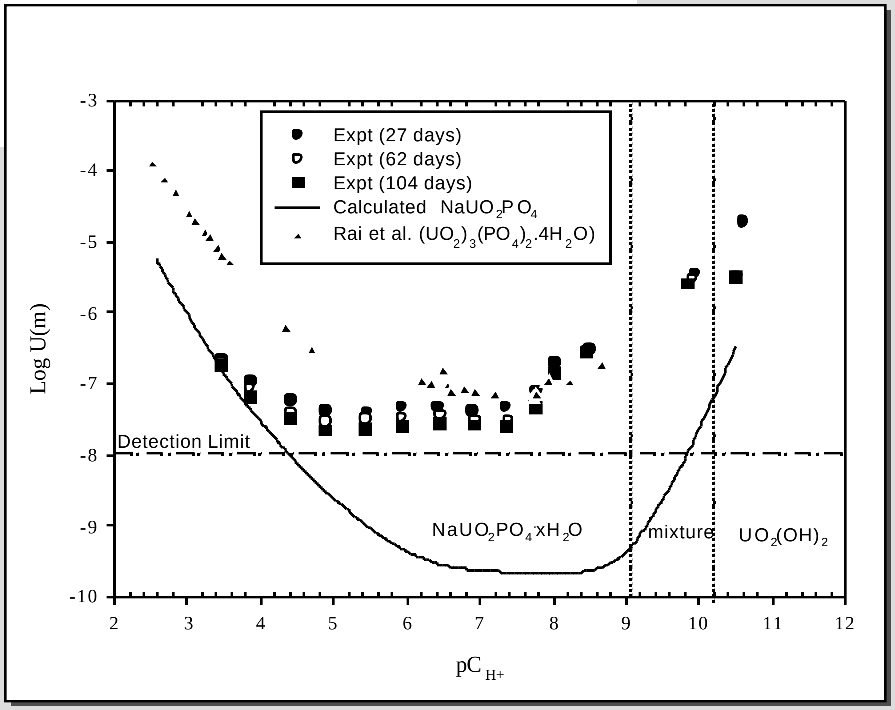


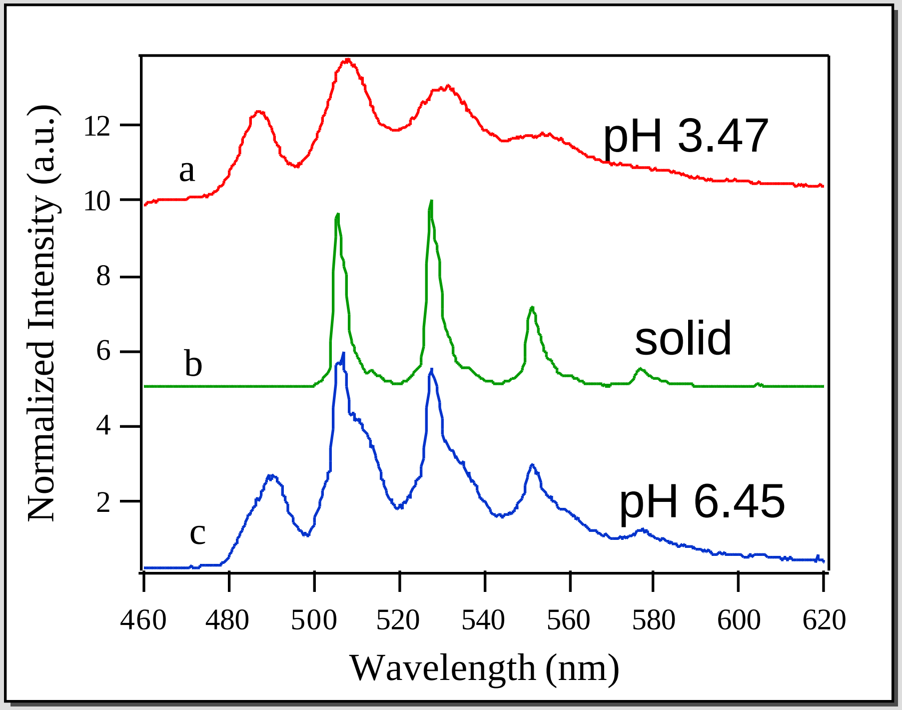
Present in fluorescence spectra

Structurally complex is completely coordinated with silca or nitrate, contains no waters of hydration, and it formation correlates with the formation of polysilicates in solution.

Z. Wang, A. R. Felmy and Y.X. Xia, O. Qafoku, W. Yantassee and H. Cho (**2004**) "Complexation Of Cm(III)/Eu(III) With Silicate In Basic Solutions", *Radiochimica Acta*, (submitted).

U(VI)-Carbonate Complexation and U(VI)-Phosphate Solubility (Presence of nanoparticles in filtered solutions)





$NaUO_2PO_4.xH_2O$ solubility
($0.01M\ PO_4$ and $0.5M\ NaNO_3$)

LHT U(VI) fluorescence spectra

Solutions from pH 4.5 – 8 contained nanoparticles or trace carbonate contamination.

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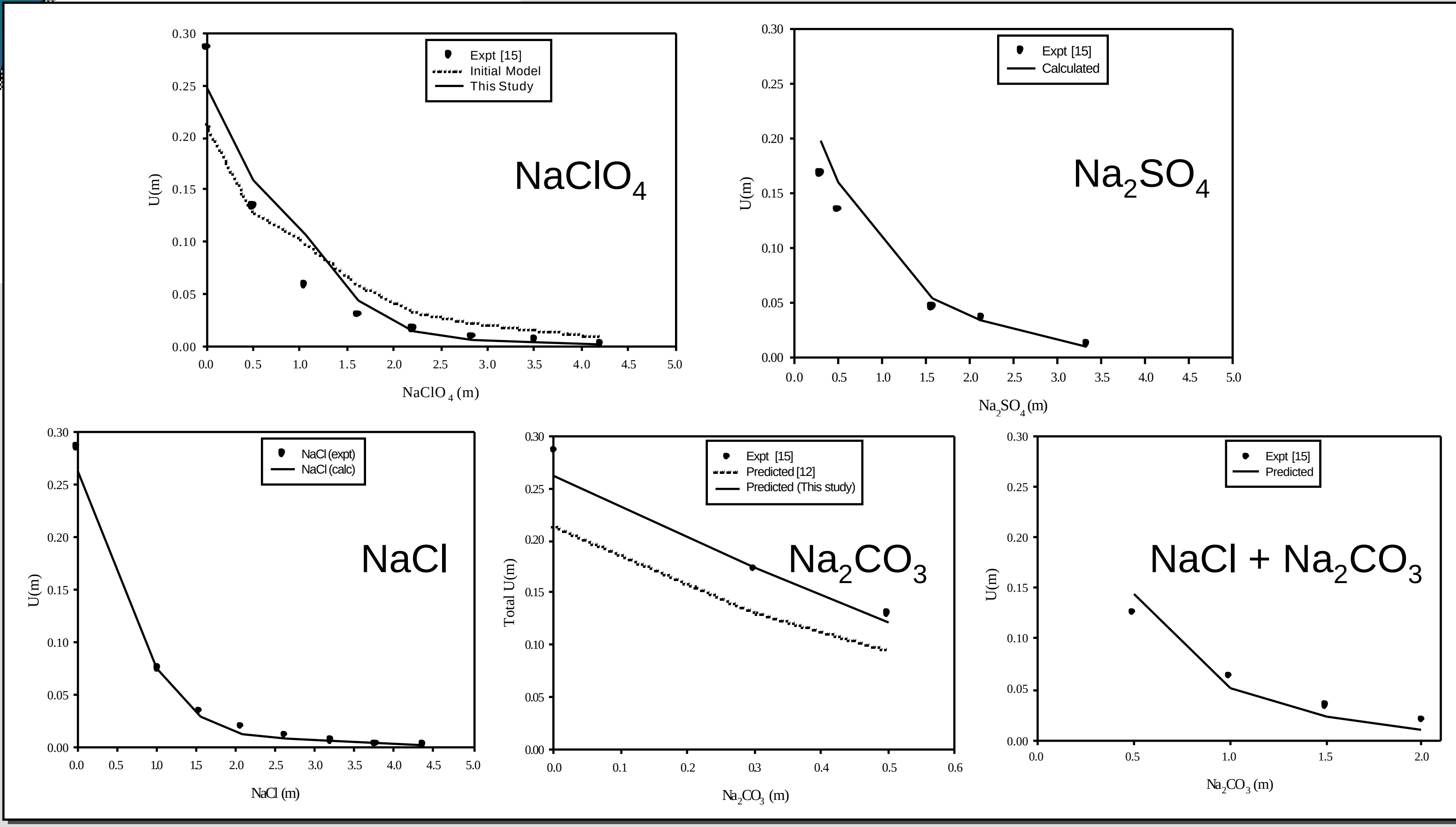
Development of Na$^+$ Ion-interaction Parameters with U(VI)-carbonate Complexes



Also tested on Cejkaite solubilites from C-203.

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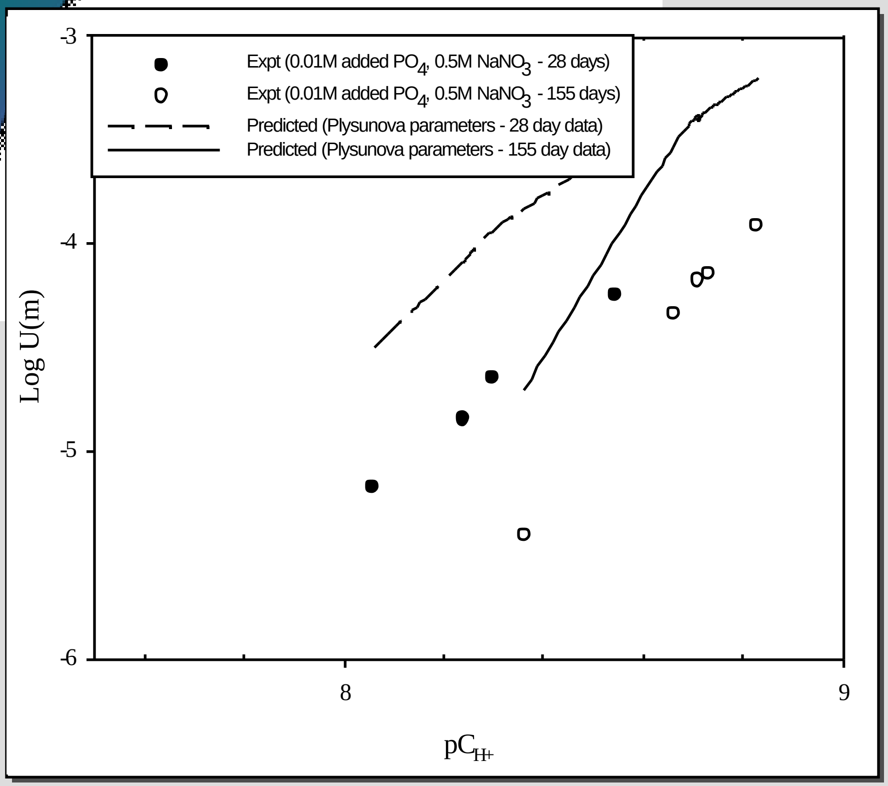
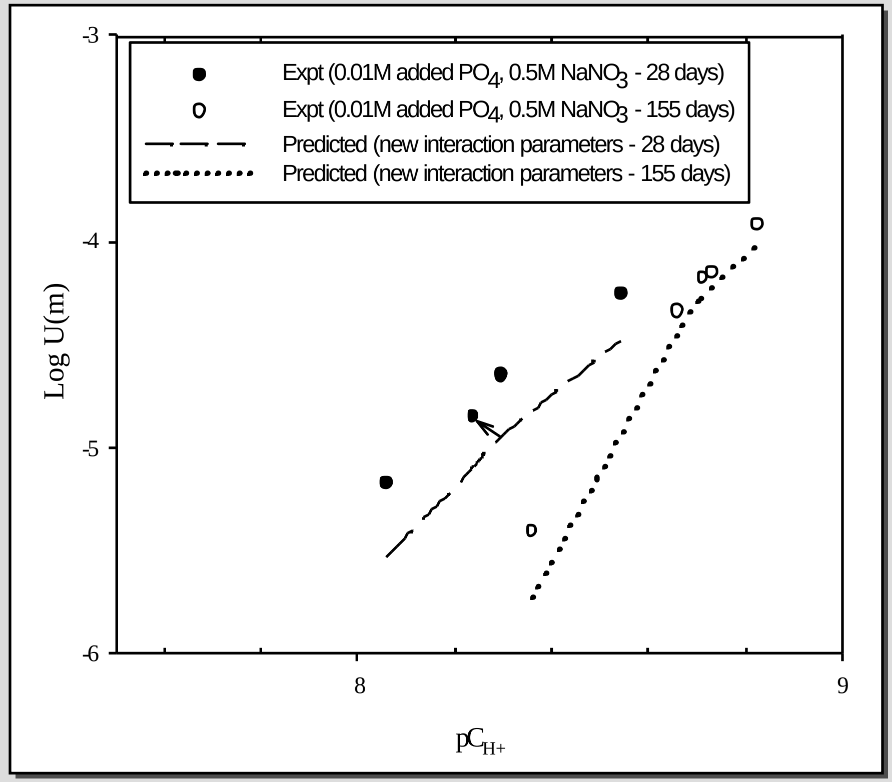
$NaUO_2PO_4$ Solubility in Carbonate Solutions



Before



After

Reason for the initial lack of agreement for the solubility of $NaUO_2PO_4$(c) in carbonate solutions was do to a poor aqueous thermodynamic model.

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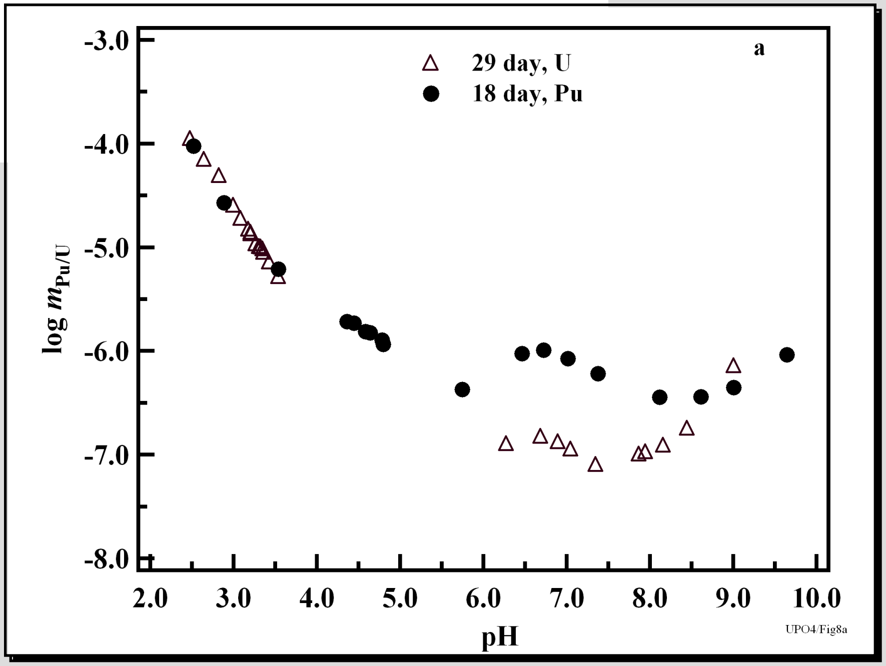
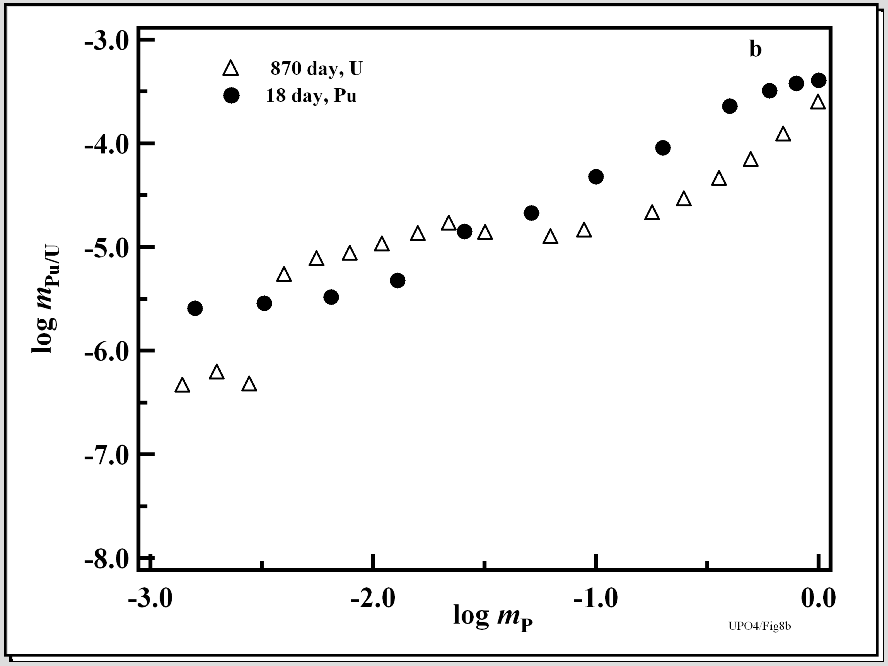
Comparison between U(VI) and Pu(VI) Solubilities

$(UO_2)_3(PO_4)_2.4H_2O$ and $(PuO_2)_3(PO_4)_2.4H_2O$



Variable pH – 0.01m PO_4



Fixed pH – Variable PO_4

Felmy, A.R., Y. Xia, and Z. Wang. "The Solubility Product of NaUO2PO4.xH2O Determined in Phosphate and Carbonate Solutions". Radiochimica Acta (submitted).

Rai, D., Y. Xia, L. Rao, N.J. Hess, A.R. Felmy, D.A. Moore, and D.E. McCready. Solubility of (UO2)3(PO4)2.4H2O in H+-Na+-OH--H2PO4--HPO42--PO43--H2O and its Comparison to the Analogous PuO22+ System. Journal of Solution Chemistry (accepted).

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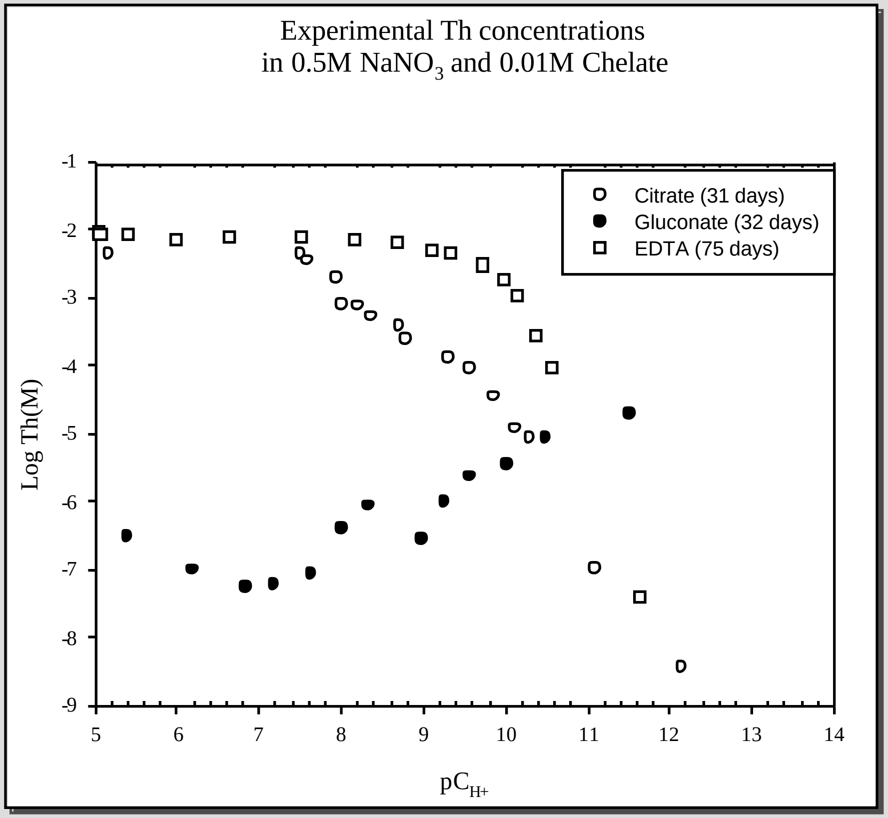
Actinide-chelate Complexation

- Evaluated the complexation reactions for Sr and trivalent and tetravalent actinides to high base and high ionic strength for several chelates (EDTA, HEDTA, citrate, and gluconate).
  - Also evaluated the competing metal ions Ca and Ni with EDTA.
  - Data used in several applications in the pretreatment area.



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Publications

- Felmy, A.R., and O. Qafoku (2004). An Aqueous Thermodynamic Model for the Complexation of Nickel with EDTA Valid to High Base Concentration. *Journal of Solution Chemistry*: 33(8), 1159-1178.

- Xia, Y., A.R. Felmy, L. Rao, Z. Wang, and N.J. Hess (2003). Thermodynamic Model for the Solubility of ThO2(am) in the Aqueous Na+-H+-OH--NO3--H2O-EDTA system. *Radiochimica Acta,* 91(12):751-760.

- Felmy, A.R. and M.J. Mason (2003). An Aqueous Thermodynamic Model for the Complexation of Sodium and Strontium with Organic Chelators valid to High Ionic Strength. I. Ethylenedinitrilotetraacetic acid (EDTA). *Journal of Solution Chemistry*; 32(4), 283-300

- Felmy, A.R., M.J. Mason and O. Qafoku (2003). An Aqueous Thermodynamic Model for the Complexation of Sodium and Strontium with Organic Chelators valid to High Ionic Strength. II. N-(2-hydroxyethyl)ethylenedinitrilotriacetic acid (HEDTA*). Journal of Solution Chemistry*; 32(4), 301-318.

- Felmy, A.R., H. Cho, D.A. Dixon, Y. Xia, N.J. Hess, and Z. Wang. "Stoichiometry and Structure of Aqueous Thorium Citrate Complexes under Neutral to Basic Conditions". *Inorganic Chemistry* (submitted)

- Felmy A.R., M.J. Mason, O. Qafoku, and D.A. Dixon. Development of Accurate Chemical Equilibrium Models for the Hanford Tanks: The System Na-Ca-Sr-OH-CO3-NO3-EDTA-HEDTA-H2O. *EMSP Symposium Proceedings* (in press)

- Felmy, A.R., Z. Wang, D.A. Dixon, and N.J. Hess. Chemical Equilibrium Modeling of Hanford Waste Tank Processing: Applications of Fundamental Science. In *Waste Management 04 Symposium. Basic Environmental Science Issues for D&D, ER and Long-Term Stewardship in the US*. (in press).

- Felmy A.R. and G.T. MacLean (FFS) (2003). Thermodynamic Modeling of AZ-101 Slurry Leaching. PNWD-3289, WTP-RPT-067 Rev 0, Final Report. Prepared for Bechtel National Inc. by Battelle Pacific Northwest Division.

- Rapko B.M., I.E. Burgeson, H. Cho, J. Deschane, A.R. Felmy, E Jenson, B.K. McNamara, A.P. Poloski, L. Snow, and G.T. MacLean (2003). Mixing of WTP Process Solutions. WTP-RPT-080, Rev 0. Prepared for Bech[illegible] Battelle Pacific Northwest Division.

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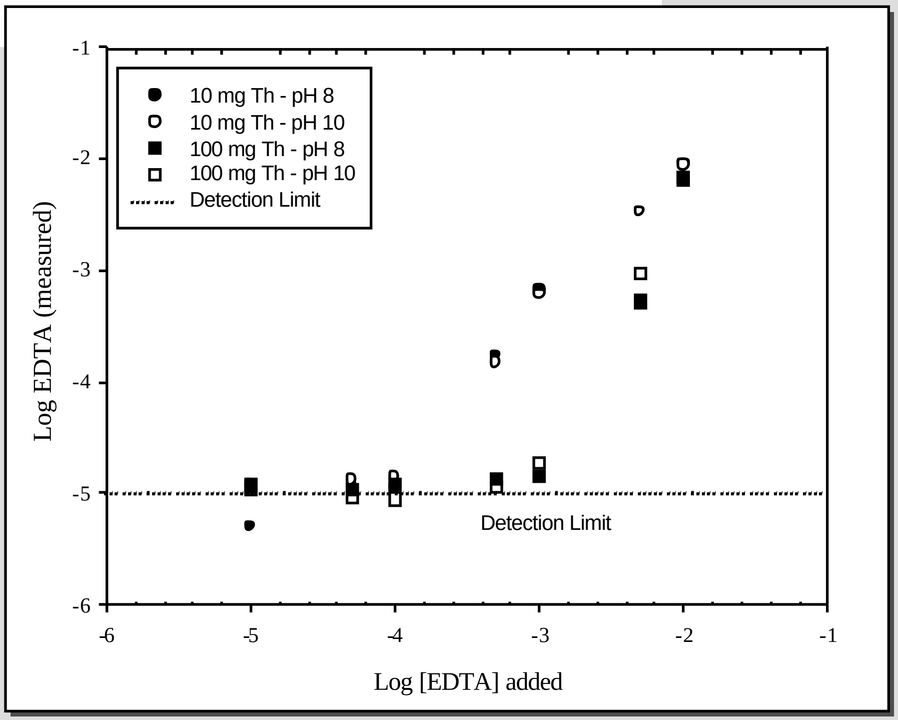
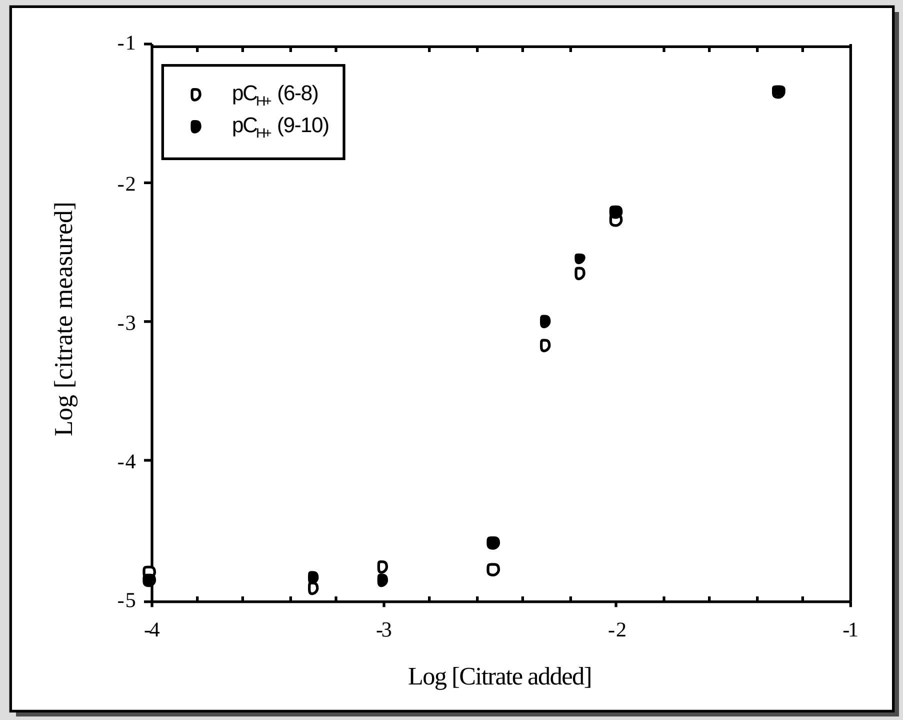
Adsorption of Chelates/Metal-chelate Complexes

- First noted in our actinide hydrous oxide solubility studies (Ex: Hydrous ThO_2).
- Limits the range of chelate/metal concentrations that can be examined by solubility measurements.



EDTA



Citrate

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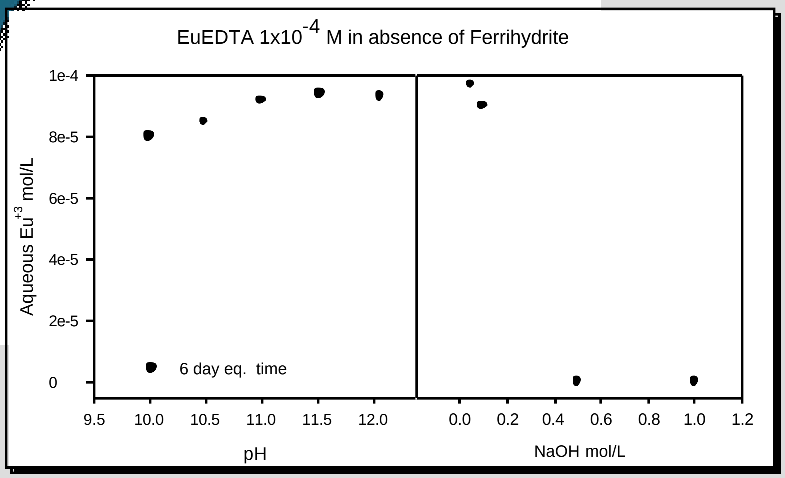
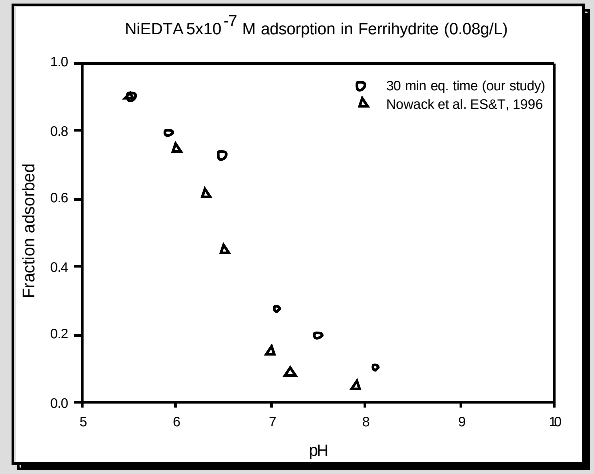
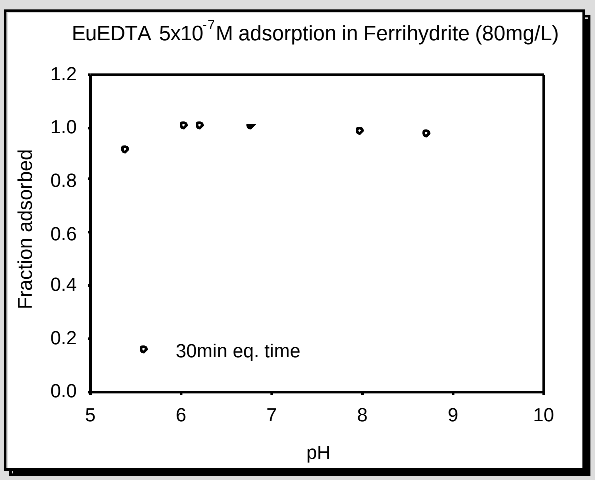
EuEDTA Adsorption to Ferrihydrite
(Collaborations with S.B. Clark [WSU])



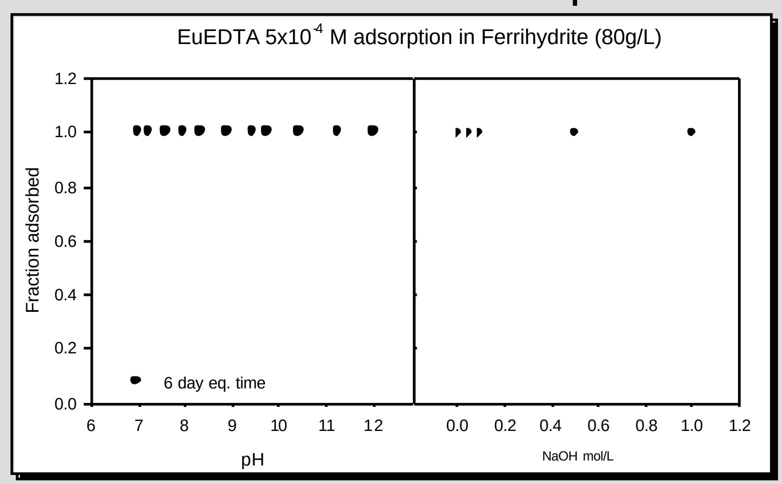
No Ferrihydrite



NiEDTA – literature comparison



EuEDTA – 80mg/l solid



EuEDTA – 80g

Impacts subsurface and tank residual areas

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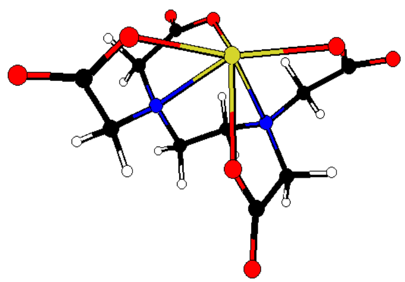
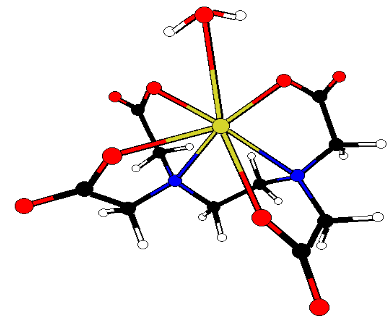
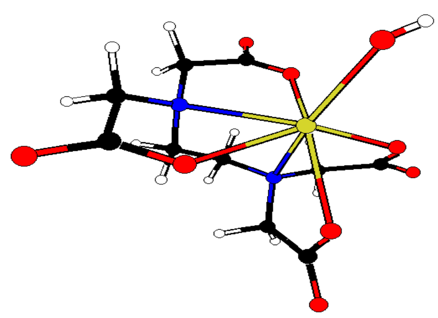
Molecular Simulations of LaEDTA Complexes



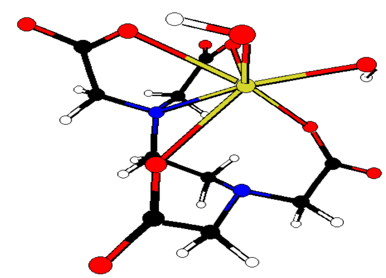
$LaEDTA^-$



$La(H_2O)EDTA^-$



$LaOHEDTA^{2-}$



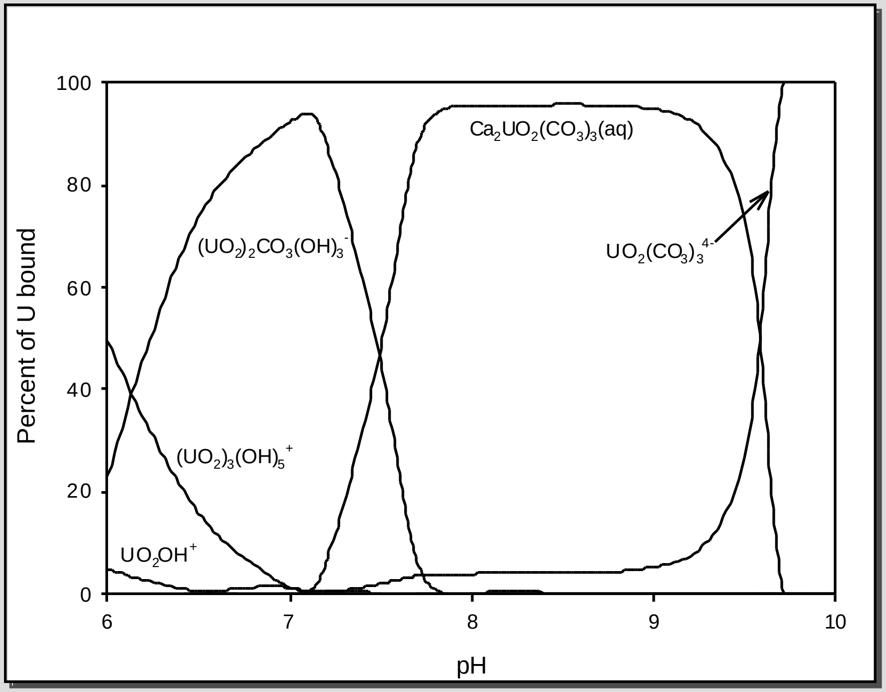
$La(OH)_2EDTA^{3-}$

Future Research Directions

- Divalent metal – actinide – carbonate complexation.
  - Example: $Ca_2UO_2(CO_3)_3$ (aq) – the most important complex in subsurface applications.
  - Thermodynamic data unreliable – not accepted in the latest NEA review.
    - Ionic strength dependence not accurately included.
    - Data limited to one pH.
    - Experiments oversaturated with respect to calcite.
    - Nature of complexes not known.
  - No data for other important complexes (Mg – $UO_2(CO_3)_3^{4-}$, Sr – $UO_2(CO_3)_3^{4-}$ or other actinides).
  - Found in Hanford groundwater.
  - Impacts microbial reduction of U(VI).

Future Research Directions

- Divalent metal – actinide – carbonate complexation.
  - Have a model for the ionic strength dependence.
  - Molecular simulations of complexes in solution.
  - Direct tie to reactive transport models.



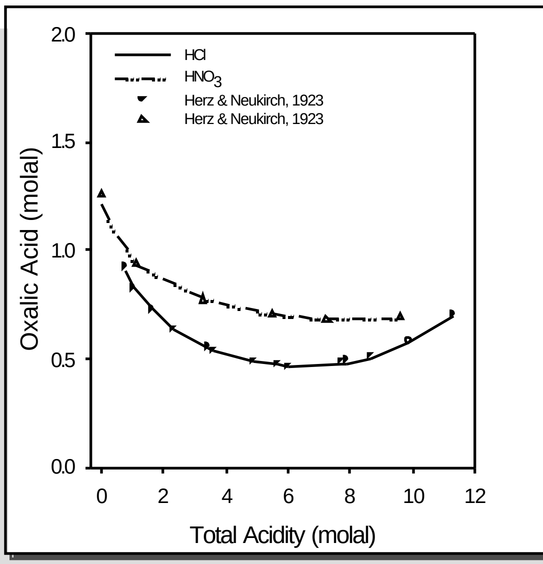
Current speciation diagram

Future Research Directions

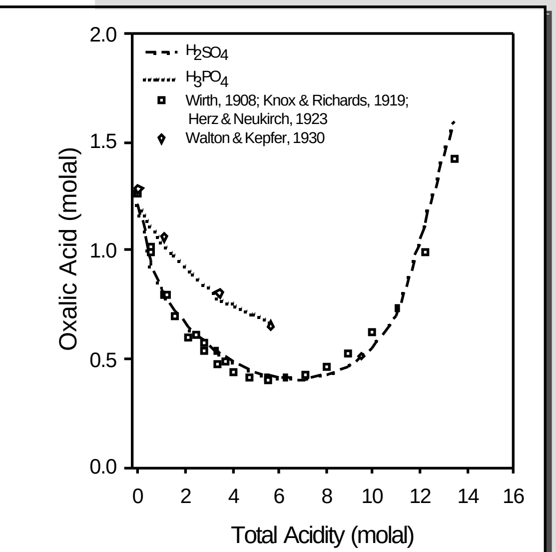
- Chelate Complexation
  - Focus on oxalate/oxalic acid.
    - Many of the tanks saturated with respect to sodium oxalate.
      - Modeling the influence of oxalate important.
    - Oxalic acid has been used in tank retrieval (C-106).
      - Future use unknown.
  - Progress
    - Great deal of past research.
      - Unify this body of information into a useful thermodynamic model valid over a range of ionic strengths and acid/base concentrations.
      - Completed a model for oxalic acid in different electrolytes.
      - Extended to higher base concentration.
        - Fitting the apparent K's for bioxalate and oxalate species in sodium containing electrolytes.

Future Research Directions

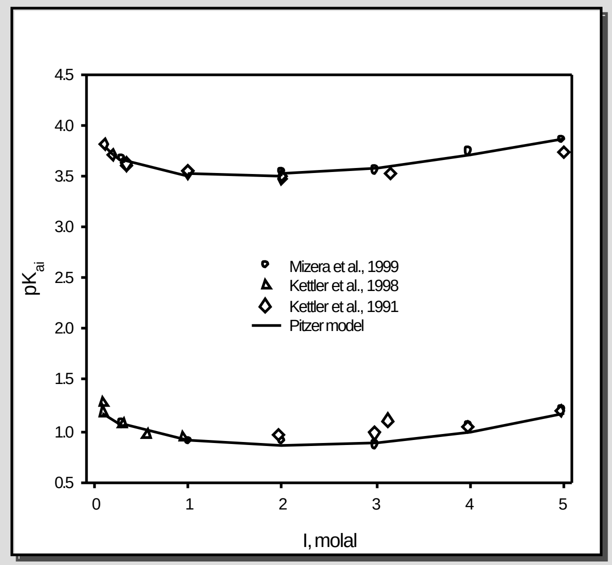
- Progress on $H_2Ox(aq)$ - HOx^- - Ox^{2-} -H_2O system.



HCl and HNO_3



H_2SO_4 and H_3PO_4



pKa values in NaCl

Summary

- Significant progress in subsurface and HLW areas
  - New trivalent actinide – silica complex(s) at high pH.
  - New thermodynamic models.
    - U(VI) phosphate phases.
    - U(VI) carbonate species ionic strength dependence.
    - Actinide chelate complexes (Sr, trivalent and tetravalents with EDTA, HEDTA, citrate, gluconate).
- New directions
  - Divalent metal – actinide –carbonates.
  - Oxalate speciation in tank solutions.
  - Actinide-chelate complex adsorption to solids.