

Title: The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica and Uranium Species to High Concentration.

Project Number: 30944

Name of Laboratory: Pacific Northwest National Laboratory

PNNL Principal Investigator: ANDREW R. FELMY

Problem Statement and Research Objective

Highly basic tank wastes contain several important radionuclides, including ^{90}Sr , ^{99}Tc , and ^{60}Co , as well as actinide elements (i.e., isotopes of U, Pu, and Am). These highly basic tank wastes are known to have leaked into the vadose zone at the Hanford Site. Upon entering the sediments in the vadose zone, the highly basic solutions dissolve large concentrations of silica from the silica and aluminosilicate minerals present in the subsurface. These dissolution reactions alter the chemical composition of the leaking solutions, transforming them from a highly basic (as high 2M NaOH) solution into a pore solution with a very high concentration of dissolved silica and a significantly reduced pH. This moderately basic (pH 9 to 11), high-silica solution has the potential to complex radionuclides and move through the subsurface. Such strong radionuclide complexation is a currently unconsidered transport vector that has the potential to expedite radionuclide transport through the vadose zone. These strong complexation effects have the ability to significantly alter current conceptual models of contaminant migration beneath leaking tanks.

In this project, we are determining the aqueous thermodynamics and speciation of dissolved silica and silica-radionuclide complexes to high silica concentration. We are also initiating studies of U(VI) speciation under strongly basic conditions.

Research Progress and Implications

In FY03, we completed many of our studies on the aqueous complexation of anionic silica species with important metal ions and radionuclides and initiated an experimental program examining the chemistry of uranium under high ionic strength conditions. During this FY these studies have focused on examining the complexation of Co(II) with aqueous silica species and the formation of U(VI) phosphate phases.

Co(II) – silica complexation

As part of this project colleagues at Florida State University (G. Choppin) have determined the stability constants for Co(II) with monomeric silica species. In these studies we evaluated the hydrolysis species of Co(II) valid to high base concentration and developed an improved second hydrolysis constant for the neutral $\text{Co}(\text{OH})_2(\text{aq})$ species. In addition we tested the solutions for the possible formation of Co(II) complexes with polysilicate species that could be present in the

subsurface under basic conditions. In the latter case we found no evidence for Co(II) polysilicate formation. As an example, Figure 1 shows the solubility of a 1:1 Co:Si containing phase which has been spiked with different concentrations of silica ranging from 10^{-4} to 0.05M. In no case did the solubility of the precipitated silica phases increase, even though the aqueous silica concentrations increased by several orders of magnitude. Such findings are important in that it appears that the high concentrations of aqueous silica that can be present under basic conditions in the subsurface will be ineffective in mobilizing radionuclides such as ^{60}Co . We are currently examining the Co:Si precipitates with XPS to better determine the near-surface Co:Si ratios and unravel the mechanisms of dissolution.

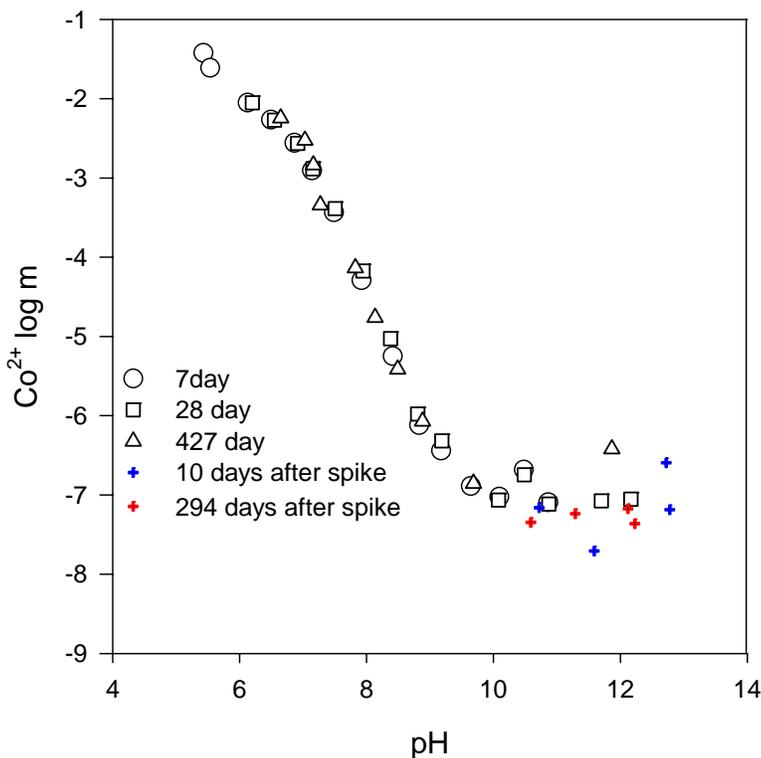


Figure 1. The solubility of a 1:1 Co:Si phase as a function of pH and added aqueous silica.

U(VI) phosphates

$\text{NaUO}_2\text{PO}_4(\text{c})$ was a well known component (the so called “hard sludge”) in the Hanford tank sludges resulting from neutralization of wastes from the bismuth phosphate process. The phase is also known to quite insoluble under circumneutral pH values in the presence of sodium concentrations greater than 0.1M. $\text{NaUO}_2\text{PO}_4(\text{c})$ is thus of primary importance in tank sludges and in determining the solubility of uranium in the subsurface in the vicinity of waste leaks containing uranium. Unfortunately, accurate solubility products for this material are currently unavailable owing both to the difficulties in phase identification and in calculating solubility products for solutions where multiple U(VI)-phosphate species maybe present in solution. We have therefore undertaken a systematic study of the solubility reactions of $\text{NaUO}_2\text{PO}_4(\text{c})$.

An example of our initial data on the solubility of $\text{NaUO}_2\text{PO}_4(\text{c})$ is shown in Figure 2. Of primary emphasis is the low solubility of U(VI) species being maintained by $\text{NaUO}_2\text{PO}_4(\text{c})$. This clearly shows that this phase is a likely solubility controlling solid phase for U(VI) in the waste tank leachates. Also of interest are the solubility data for the normal uranium phosphate $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ obtained by previous investigators. There is obviously a large discrepancy in these values even though both investigators claim the equilibrium solid phase is the normal uranium phosphate. It is also of interest to point out that fluorescence measurements of the aqueous species present in contact with the $\text{NaUO}_2\text{PO}_4(\text{c})$ solid are strictly hydrolysis species of U(VI), in contrast to the predictions of current thermodynamic models. A manuscript summarizing these results is currently in preparation.

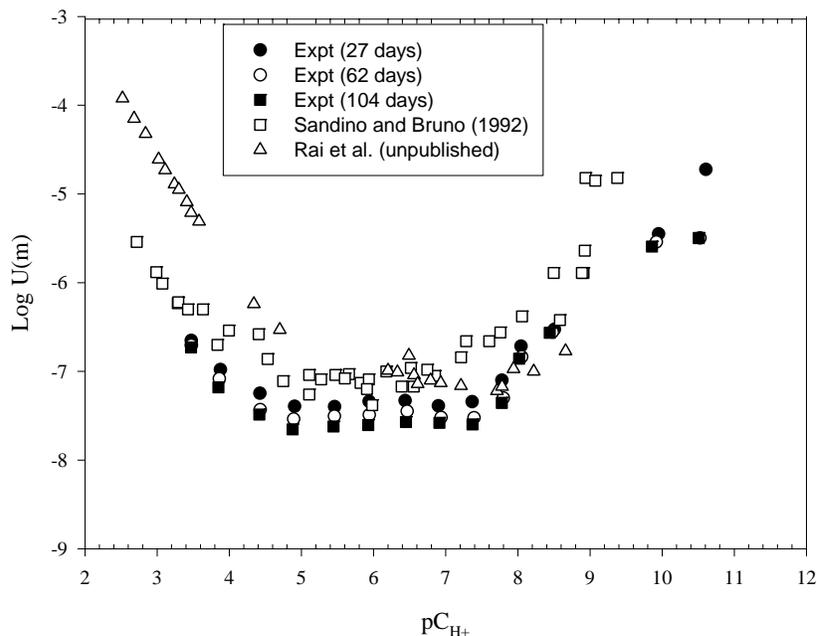


Figure 2. The solubility of different uranium containing solid phases in the $\text{Na}^+ - \text{UO}_2^{2+} - \text{H}^+ - \text{PO}_4^{3-} - \text{H}_2\text{O}$ system.

We also created another version of our Pitzer thermodynamic model database for use in reactive transport modeling and other applications. One of these applications was examining the possible effects of colloid formation in Hanford sediments in collaboration with colleagues at Washington State University.

Publications

Rai, D., N.J. Hess, M. Yui, A.R. Felmy, and D.A. Moore. "Thermodynamics and Solubility of $(\text{U}_x\text{Np}_{1-x})\text{O}_2(\text{am})$ Solid Solution in the Carbonate System." *Radiochimica Acta* (in press).

Felmy A.R., M.J. Mason, O. Qafoku, and D.A. Dixon. Development of Accurate Chemical Equilibrium Models for the Hanford Tanks: The System $\text{Na} - \text{Ca} - \text{Sr} - \text{OH} - \text{CO}_3 - \text{NO}_3 - \text{EDT} - \text{HEDTA} - \text{H}_2\text{O}$. EMSP Symposium Proceedings (in press).

Mashal, K., J.B. Harsh, M. Flury, and A.R. Felmy. "Colloid Formation in Hanford Sediments Reacted with Simulated Tank Waste". *Environmental Science and Technology* (accepted).

Felmy, A.R., M.J. Mason, P.L. Gassman, and D.E. McCready. (2003). "The Formation of Strontium Silicates at Low Temperature and the Solubility Product of Tobermorite like $\text{Sr}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$." *American Mineralogist* 88(1):73-79.

Lichtner P.C., and A.R. Felmy. (2003). "Estimation of Hanford SX Tank Waste Compositions from Historically Derived Inventories." *Computers & Geosciences* 29(3):371-383.

Wang, Z., A.R. Felmy, Y. Xia, and M.J. Mason. (2003). "A Fluorescence Spectroscopic Study on the Speciation of Cm(III) and Eu(III) in the Presence of Organic Chelates in Highly Basic Solutions." *Radiochimica Acta* 91:329-337.