Development of Accurate Chemical Equilibrium Models for the Hanford Waste Tanks: New thermodynamic measurements and model applications.

Andrew R. Felmy, Marvin Mason, Odeta Qafoku, Yuanxian Xia, Zheming Wang
The Pacific Northwest National Laboratory, Richland WA

Graham MacLean
Fluor Federal Services, Richland WA

High-level radioactive waste tanks at U.S. Department of Energy (DOE) storage sites contained, or are suspected to have contained, significant concentrations of radioactive species, including actinide elements. The high ionic strength and highly basic conditions of the waste tanks, combined with the presence of strong chelating agents in some of the most critical tanks for immediate processing makes developing accurate thermodynamic models to predict the chemical behavior of the tanks an extremely daunting challenge in electrolyte and radionuclide chemistry. Such predictive thermodynamic models are needed to improve waste tank processing strategies and the transport of radionuclides through the subsurface in the vicinity of a tank leak.

In the is presentation the current status of these thermodynamic models will be reviewed with emphasis placed on the most important radionuclides which effect current waste processing strategies being examined by the Waste Treatment Plant/River Protection Project and the Hanford Vadose Zone Science and Technology (HVZS&T). Recent applications of new thermodynamic models developed under the EMSP program to the processing of wastes from tank AZ-101 will also be presented.

As an example, Sr-90 is a key radionuclide in the processing of the current high priority tanks at Hanford (AN-107, AN-102, AZ-101) and is also an important radionuclide, which may have leaked from the waste tanks currently being investigated by the HVZS&T. In order to develop an accurate thermodynamic model to predict the chemical behavior of Sr-90 we systematically studied the reactions of Sr with the most important inorganic (hydroxide and carbonate) ligands and organic (EDTA, HEDTA) chelators in the tanks. These systems were studies over a broad range of ionic strengths and temperatures. One of the key aspects of these studies was the use of molecular modeling (based upon density functional theory, DFT) to correlate binding energies for gas phase complexes with solution phase equilibrium constants. This ability was of particular importance when attempting to determine the possible species present in solution under conditions, such as low total dissolved concentration, when direct spectroscopic or other measurements was impossible. Figure 1, shows examples of the solubility data for $SrCO_3$(c) and $CaCO_3$(c) in Na_2CO_3 solutions which indicated the presence of previously unidentified $Sr(CO3)_2^{2-}$ and $Ca(CO3)_2^{2-}$ complexes. The calculated stability constants for these complexes from the data shown in Figure 1 were then shown to correlate well with the known stability constants for other Ca and Sr complexes based upon their DFT binding energies, Figure 2.

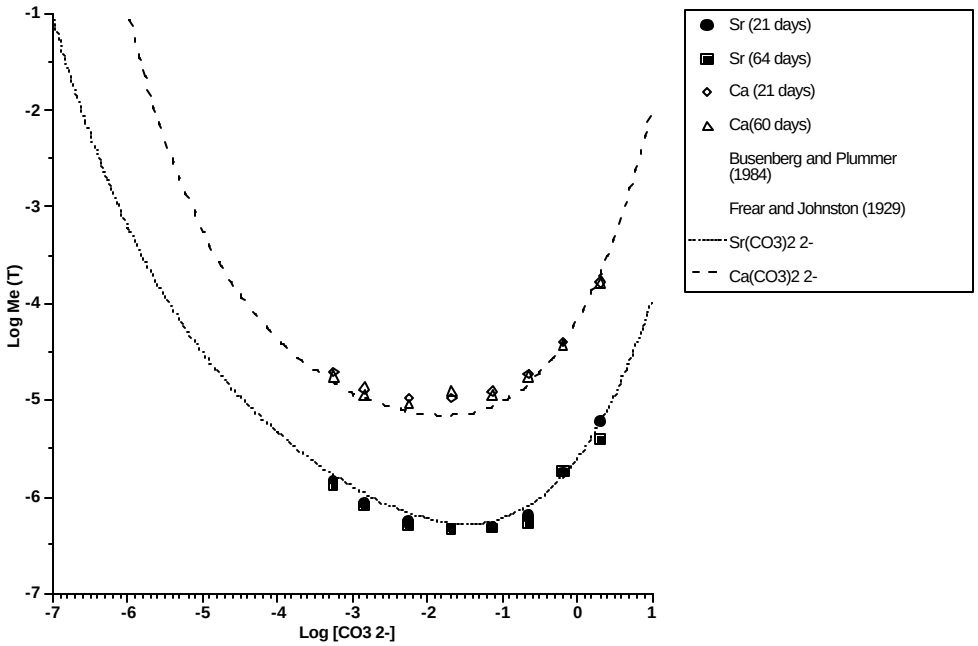

Figure 1. Experimental and calculated Sr and Ca concentrations in equilibrium with $SrCO_3$ and $CaCO_3$ respectively. Model calculations assume the formation of dicarbonate Ca and Sr complexes. From Felmy et al. (1998).

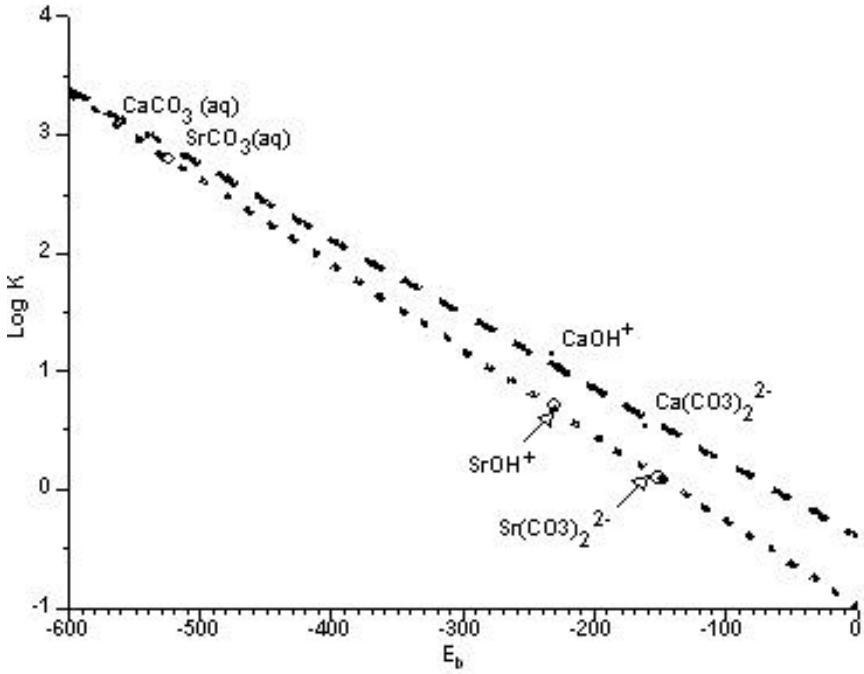

Figure 2. Correlation between solution phase equilibrium constants and DFT binding energies for Ca and Sr aqueous complexes.

Once the inorganic speciation of Sr was unraveled, as described above, our studies turned to the organic chelates EDTA and HEDTA. These ligands are the two principal organic chelates for Sr-90 present in the Envelope C waste tanks at Hanford. Understanding their aqueous complexes with Sr under high ionic strength and high base concentration is the key factor in unraveling the Sr/TRU precipitation process being implemented by Bechtel National at Hanford (Felmy 2000). In the Sr/TRU process, stable Sr is added to the waste in order to precipitate $SrCO_3$ from the concentrated carbonate containing solutions via isotopic substitution. Not surprising one of the key factors in the success or failure of this method is in accurately predicting the solubility of $SrCO_3$ in the presence of the organic chelates. As part of our EMSP project, we developed the necessary thermodynamic data to predict these solubilities over the temperature range 25 to 75^0C, from 0.01m to 2.0m Na_2CO_3, and extending to an ionic strength of 9. Examples of our final thermodynamic model are shown in Figures 3 and 4. From a scientific perspective, these studies provided the first definitive values for the standard state equilibrium constants for SrEDTA complexes, as opposed to the commonly used 0.1M reference state values.

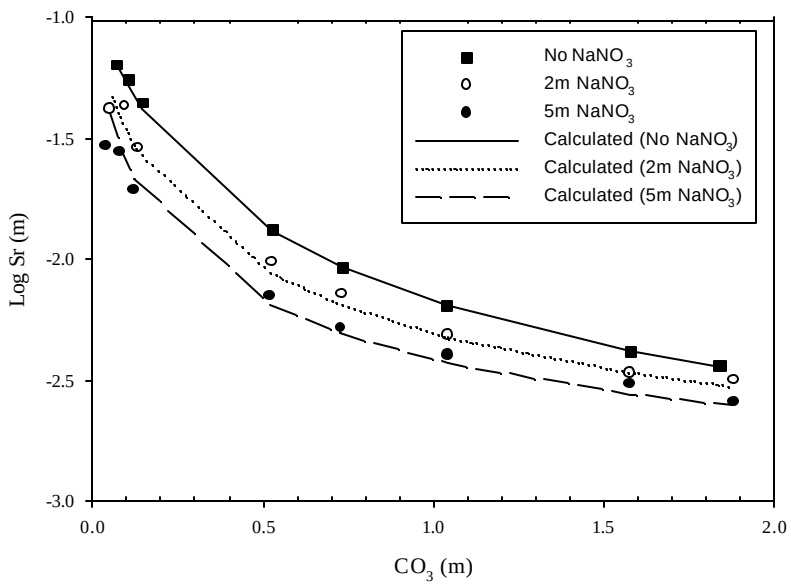

Figure 3. Experimental and Calculated Solubilities of $SrCO_3$ as a function of Na_2CO_3 concentration and in the presence of EDTA and different concentrations of $NaNO_3$. From Felmy et al. (2002).

The other key factor in predicting the aqueous chemistry of Sr in the tank waste solutions is to unravel the effects of competing metal ions. Certain metal ions present in the waste tanks (principally Ca and Ni) have a higher affinity for the organic chelates than Sr. These metals thus have the ability to displace Sr from the coordination sphere of the organic complexes. As a result, unraveling the chemical behavior of these competing metals is as a key to predicting the aqueous chemistry of Sr in the waste tanks. We have only recently initiated studies of these competing metal ions. Example results for the competing metal Ca are shown in Figure 4.

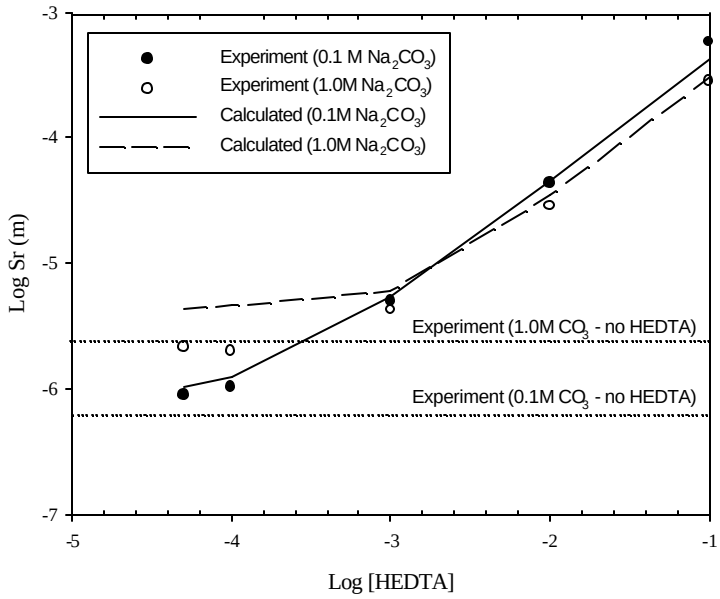

Figure 4. Experimental and calculated $SrCO_3$(c) solubilities as a function of HEDTA concentration in the presence of $CaCO_3$(c). From Felmy et al. (2002b).

In addition, in conjunction with OLI Systems Inc., we have also developed a software program for tracking the thermodynamic data used in our modeling of Hanford tank waste. This software, OLI DATATRACKER (Sanders et al. 2001), is a key in the trace ability and scientific credibility of the thermodynamic database developed under funding support from EMSP. Examples of how this software program works will be presented.

Finally, it is important to note that the tank waste chemistry serves as the effective source term for modeling all subsurface transport of tank waste. As a result, the thermodynamic database presented here is also being used by the HVZS&T program in their reactive transport simulations (Lichtner et al. 2002).

References

Felmy, A.R., D.A. Dixon, J.R. Rustad, M.J. Mason, and L.M. Onishi. (1998). "The Hydrolysis and Carbonate Complexation of Strontium and Calcium in Aqueous Electrolytes: Use of Molecular Modeling Calculations in the Development of Aqueous Thermodynamic Models." *Journal of Chemical Thermodynamics* **30,** 1103-1120.

Felmy, A.R., and M.J. Mason. (1998). "The Displacement of Sr from Organic Chelates by Hydroxide, Carbonate, and Calcium in Concentrated Electrolytes." *Journal of Solution Chemistry* **27**(5):435-454.

Felmy A.R. (2000). Thermodynamic Modeling of Sr/TRU Removal. PNWD-3044, BNFL-RPT-037 Rev 0.

Felmy A.R. and G.T. MacLean. (2001). Development of an Enhanced Database for the ESP Model: The Fluoride and Phosphate Components. WTP-RPT-018 Rev. 0.

Felmy, A.R. and M.J. Mason. (2002a). "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* (in review).

Felmy, A.R., M.J. Mason, and O. Qafoku. (2002b). "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* (in review).

Lichtner, P.C., and A.R. Felmy. (2002). "Estimation of Hanford SX Tank Waste Compositions from Historically Derived Inventories." *Computers & Geosciences.* Special issue on Reactive Transport Modeling in the Geosciences (accepted).

Sanders, S, R. Young and A.R. Felmy. (2001). Inclusion of Pitzer Equations in the ESP Computer Model (Beta Version). Tanks Focus Area Milestone Report B.3-1 (September 2001).