Thermodynamic Models for Multivalent Actinide Solubility and Speciation as a Function of Temperature and Ionic Strength

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ABSTRACT:

Actinide release is a critical performance measure for a geologic repository, and there are several potential pathways for actinide release that must be considered in a performance assessment. In all cases, it is important to determine the actinide source term, which is defined by aqueous-phase speciation and the identity and dissolution rate of solubility-controlling phases, and relies on variables such as actinide oxidation state, the presence and concentration of complexing or competing ions, and the geochemical boundary conditions of the repository. Most experiments targeted at understanding actinide solubility and speciation have been performed at 25 °C and relatively low ionic strength ($I \leq 0.1$ m). However, geologic repositories will have elevated temperatures and/or ionic strengths. Because the predictive power and accuracy of geochemical and reactive transport models rely on robust thermodynamic datasets, the temperature and ionic-strength dependence of thermodynamic constants must be known in order to make accurate predictions of actinide transport.

Several methods exist to approximate the effect of temperature and ionic strength on solubility and speciation. Because ionic solutions depart from reality due to long-range electrostatic interactions, different approaches are used to determine the ionic strength dependencies of chemical equilibria (e.g., Specific Ion Interaction Theory (SIT), Pitzer models). While many SIT parameters are available in the literature, their variability with temperature is unknown. Significantly fewer Pitzer parameters are known, particularly for actinide ions; often extrapolations are made from known values. The approaches commonly used to determine the temperature dependencies of chemical equilibrium require that the enthalpy, entropy, and/or heat capacity of the given reaction is known, yet these values are rarely available for actinide systems. The limitations of approximation approaches, such as using the van't Hoff equation to extrapolate the effect of temperature on the complexation constant for a reaction, and lack of available data in thermodynamic databases, highlights the need for reliable experimental data on the complexation of actinides in solution at temperatures, ionic strengths, and pH values expected in a geologic repository.

The proposed project will quantify the solubility and speciation of Np and Pu under temperatures (T = 25–95 °C), ionic strengths ($I = 0.1$–10 m), and pH values ($\text{pH}_i = 5$–12) that are relevant to the generic repository concept. We aim to determine conditional K_{sp} or β values using bulk solubility experiments and UV-vis-NIR spectrophotometry, respectively, and conditional $\Delta_r H_m$ values using reaction calorimetry. Through the application of SIT and Pitzer approaches, we will be able to calculate all four thermodynamic values (i.e., log K_{sp}^0 or log β^0, $\Delta_r G_m^0$, $\Delta_r H_m^0$, and $\Delta_r S_m^0$), resulting in a full thermodynamic description of each system. As such, the proposed research addresses the DOE-NE mission-supporting goal to "secure and maintain our nuclear fuel cycle" by developing a sound technical basis for the disposal of spent nuclear fuel and wastes from the nuclear energy enterprise.