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Using Thermodynamic Models: Saline systems

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Thermodynamic models of saline systems are needed to support ongoing and future nuclear waste repository concepts in salt. These models are currently being applied to support the safety case for the Waste Isolation Pilot Plant (WIPP) which is an operating TRU waste repository in bedded salt in Southeastern New Mexico (USA). Continued model development is also needed to address potential contaminant subsurface issues (e.g., deep US aquifers) and evaluate the utility of future salt-based nuclear waste repository concepts (e.g., Gorleben in Germany).

The brine chemistry that typifies these sites are high in ionic strength (I = ~5-6 M) and cannot be modeled using the Specific ion Interaction Theory (SIT) approach (I < 3.5 M). For this reason the Pitzer formalism (see Modeling in Aquatic Chemistry, OECD, ISBN 92-64-15569-4), which is a semi-empirical approach, is used to model the radionuclide speciation and brine chemistry for these applications. There are relatively few Pitzer data available and existing data sets are currently very project/program-specific. Given the likely rise in importance of these high ionic strength systems in nuclear waste management, there is a need for a more systematic approach to the development and application of speciation models using the Pitzer formalism.

The WIPP project is the only repository program that has an existing Pitzer-based model that has been approved by their regulator (the US Environmental Protection Agency –EPA). This repository was first licensed in 1998, was recertified in 2006, and is in the late stages of getting a second recertification. Actinide solubility is modeled using the Fracture Matrix Transport (FMT) Pitzer-based model that uses a relatively small, but highly conservative, analog/actinide data set. The lessons learned from the experience of this repository program with its EPA regulator are:

- A simple, conservative, and defensible actinide speciation approach has worked the best.
- The use of oxidation-state analogs that conservatively bracket oxidation state distribution is accepted by the regulator.
- NEA databases, as they are released or updated, are impactive because they are recognized by the regulator and scientific community as a key source of peer-reviewed data. The database used within the WIPP project must address and justify differences when they exist.
- The regulator has a key and important role in the database selection process and once a license is in place it is relatively difficult to make substantial changes in the database.

The culmination of the experience in the WIPP project points to the importance of maintaining and developing radionuclide databases through the NEA process. In the specific case of saline systems, there remains a need for a more robust and self-consistent Pitzer database to more realistically model the high ionic-strength brine and actinide chemistry to support the safety case.