

The Development of Aqueous Thermodynamic Models: Application to Waste Tank Processing and Vadose Zone Issues.

The presence of a wide range of radionuclides, metal ions, inorganic ligands, and organic chelating agents combined with the high base and electrolyte concentration in the Hanford waste tanks creates some unique and difficult problems in modeling the aqueous thermodynamics of these solutions. Solving these problems is important since this can lead to better strategies for tank processing and predictions of subsurface transport. In addition, a large number of scientists and engineers at Hanford and other sites rely on these models for making accurate predictions of tank chemistry.

In developing accurate thermodynamic models for these solutions one of the most important factors is identifying the aqueous species present. Identifying these species in tank solutions presents some difficult challenges since, 1) current analytical methods for examining speciation in simple solutions, such as UV-VIS, Raman, etc., develop difficulties in interpreting or analyzing spectral features when multiple complexes are present and contribute to the observed spectra, 2) the solubility of the compounds of many elements, including the actinide elements, is very low under high base conditions. Determining the aqueous speciation in such solutions, which is still needed to predict changes in solubility, is currently done largely by curve-fitting solubility data to hypothesized speciation schemes. Clearly, new and improved approaches to this problem are needed. In order to circumvent these difficulties we have implemented a comprehensive approach which involves coupled experimental solubility studies, spectroscopic measurements of solution speciation, molecular modeling studies which yielded information on species structure and energetics, and thermodynamic modeling efforts using the Pitzer thermodynamic model which is valid to high ionic strengths. In developing this approach we have classified the speciation reactions in tank solutions into three areas: simple inorganic speciation reactions involving the addition of one or more ligands to a metal center, organic chelate binding to a metal center where the chelate completely/incompletely wraps the metal center, and systems where the binding ligand polymerizes forming multiple species which can interact with the metal ion. Examples of each of these types of reaction that effect waste tank and vadose zone applications for the actinides or fission products are described below.

The most important simple inorganic speciation reactions that can occur in these solutions involve the addition of multiple hydroxyl (owing to the high base concentration) or carbonate ligands to the metal center. For example, the addition of one carbonate ligand to the Sr^{2+} cation can result in an asymmetric complex with a strong dipole moment. Under lower base conditions, water molecules bind to the positive part of the dipole (i.e. the Sr ion) to partially neutralize the charge asymmetry. Under higher base or carbonate concentration these water molecules are replaced with either additional carbonate ligands or hydroxyl groups. In the case of Sr, hydroxyl association is very weak and the speciation is dominated by carbonate complexation. In the case of more hydrolyzable metal ions, such structural asymmetries can result in mixed complex formation. However, for larger multi-functional group organic chelates, such as EDTA or HEDTA the chelate cannot completely surround the metal center (Figure 1) which then becomes associated with hydroxyls at high base concentration. This results in the formation of metal-chelate-hydroxyl complexes that can increase the solubility of

trivalent actinide compounds by orders of magnitude in basic conditions. An example of this effect is shown in Figure 2 for the solubility of $\text{Eu}(\text{OH})_3(\text{c})$, a trivalent actinide analog. The formation of a stoichiometric EuOHEDTA^{2-} species increases the solubility by 2 to 3 orders of magnitude over predictions using a simple EuEDTA^- species. These increase in solubility and changes in speciation can dramatically effect tank processing strategies, since the desire is to retain the actinides and fission products in the sludges rather than develop costly removal strategies.

The third major type of speciation reaction involves a ligand which itself can polymerize in solution. The polymerization of the ligand results in several anionic species being simultaneously present in solution. As an example, of this type of ligand is silica which can form monomers, dimers, trimers, and tetramers in solution. All of these species are have unique binding capabilities and complexation constants with the different radionuclides. This is a current active area of research, where unique structural probes, such as NMR can distinguish the effects of cation binding to each individual complex. This specific case of silica complexation has relevance to both tank processing and vadose zone issues. Silica complexation is relevant to the vadose zone since the high base concentration, which can result from a tank leak, can dissolves silica containing minerals in the soil creating quite high dissolved silica concentrations. This dissolved silica can then form strong aqueous complexes with fission products and actinides facilitating their transport through the subsurface.

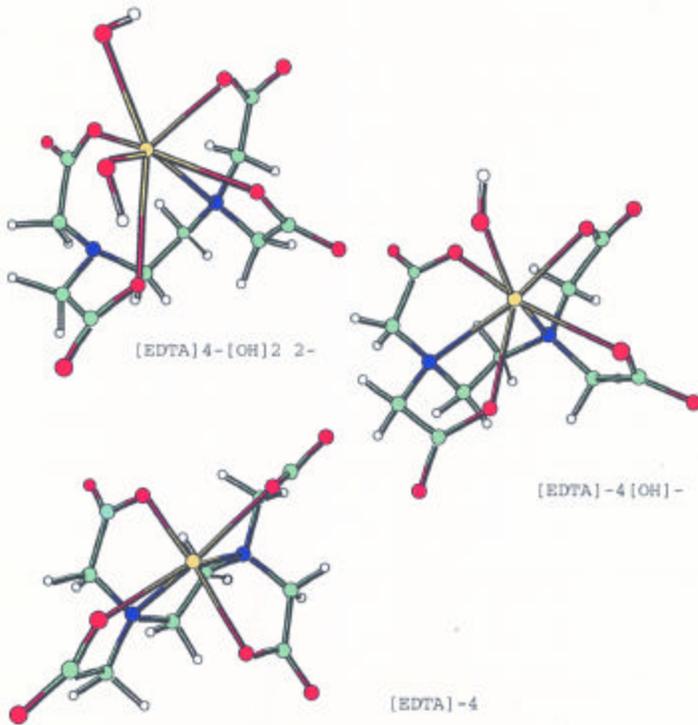


Figure 1. La-EDTA-OH clusters exhibiting the location of OH groups in the complexes.

Figure 1. La-EDTA-OH Complexes

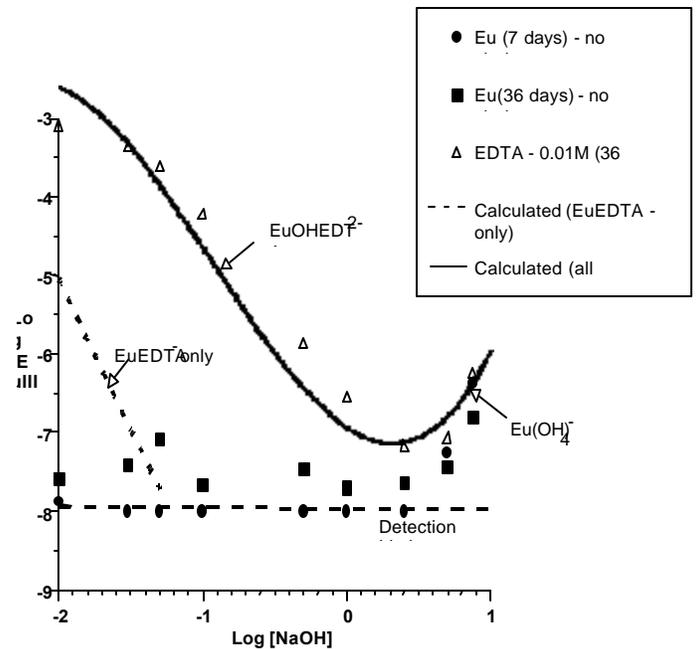


Figure 2. The effects of Eu-EDTA-OH complexation on $\text{Eu}(\text{OH})_3$ solubility at high base.

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