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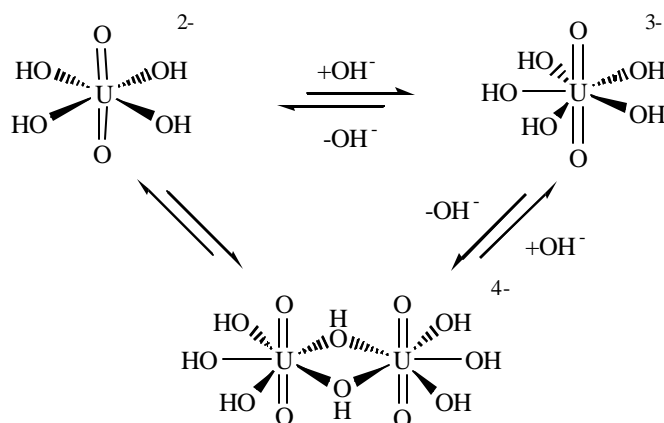
## Actinide-aluminate Speciation in Alkaline Radioactive Waste

David L. Clark

**Research Objective:** Highly alkaline radioactive waste tanks contain a number of transuranic species, in particular U, Np, Pu, and Am—the exact forms of which are currently unknown. Knowledge of actinide speciation under highly alkaline conditions is essential towards understanding and predicting their solubility and sorption behavior in tanks, determining whether chemical separations are needed for waste treatment, and designing separations processes. Baseline washing of tank sludges with NaOH solutions is being proposed to reduce the volume of HLW. Alkaline pretreatment of HLW will be needed to remove aluminum [as  $\text{NaAl(OH)}_4$ ] because it significantly reduces the HLW volume; however, the aluminate ion  $[\text{Al(OH)}_4]^-$  enhances actinide solubility via an unknown mechanism. Thus, alkaline wash residues may require an additional treatment to remove actinides.

The results of this research will determine the nature TRU (U, Np, Pu, Am) speciation with aluminate anions under alkaline, oxidizing tank-like conditions. Specific issues to be addressed include solubility of these actinides, speciation in aluminate-containing alkaline supernatants, the role of actinide redox states on solubility, and partitioning between supernatant and solid phases, including colloids. Studies will include thermodynamics, kinetics, spectroscopy, electrochemistry, and surface science. We have already determined, for example, that certain high valent forms of Np and Pu are very soluble under alkaline conditions due to the formation of anionic hydroxo complexes,  $\text{AnO}_2(\text{OH})_4^{2-}$  and  $\text{AnO}_2(\text{OH})_5^{3-}$ . The presence of aluminate ions causes the actinide solubilities to increase, although the exact species are not known. We are currently characterizing the high-valent TRU elements bound to oxo, water,  $\text{OH}^-$ , and  $[\text{Al(OH)}_4]^-$  ligands under waste-like conditions. These waste-like conditions are in the range of 1-3 M excess hydroxide, ~0.2 M carbonate, ~0.5 M aluminate, for a total sodium of 2-4 M. Molecular structure-specific probes include Raman, multinuclear nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS), luminescence, optical absorption (UV-Vis-conventional and photoacoustic) spectroscopies. We anticipate that such new knowledge will impact on clean-up approaches to significantly reduce costs, schedules, and risks.

**Research Progress and Implications:** In the first one and one half years of the project we have determined the true role of aluminate  $[\text{Al(OH)}_4]^-$  anions in enhancing solubility of actinide ions. Last year we reported preliminary spectroscopic observations of a new actinide chemical species in the presence of aluminate anions under alkaline, waste tank-like conditions. We postulated that the aluminate anion acted as a ligand to uranium, and that the new compound was an actinide-aluminate coordination complex of high negative charge. More detailed studies aimed at identification of this new species revealed that it is actually a new dimeric uranyl species, and that there is no aluminate anion in the metal coordination sphere. Rather, the data indicate that the aluminate acts as an electrolyte, and increases the hydroxide ion activity and hence the overall solubility via formation of  $\text{UO}_2(\text{OH})_5^{3-}$ . In general, highly charged species are stabilized by high ionic strength. This will have a direct impact on sludge washing using NaOH to remove aluminate ions from the system. Changes in the aluminate concentration effect the position of the equilibrium outlined below. Furthermore, we also find changes in aluminum chemistry based on the presence of uranium, including aluminate precipitation reactions under conditions where the aluminate anions should be solubilized.



**Reaction Scheme**

**Planned Activities:** The workscope for the first year was altered in order to proceed with an increased efficiency. A decision was made to limit the first year's studies to uranium in order to better characterize the equilibria identified in Scheme 1. This process has allowed us to map out the complex chemistry shown in Scheme 1 with a metal center having the most spectroscopic tags. The originally planned plutonium work is now beginning. Work will be performed to synthesize model complexes from non-aqueous solvents where the equilibria described above will no longer interfere. In addition, experiments designed to obtain crystals from aqueous solution will be performed under the conditions leading toward single species. Further studies in vibrational spectroscopy, including IR and Raman, along with  $^{17}\text{O}$ - and  $^{27}\text{Al}$ -NMR will be performed to studying the nature and thermodynamics of the equilibrium.

**Information Access:** A manuscript describing the spectroscopic data leading to the description of Scheme 1 above will be submitted for publication this summer.