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Title: ACTINIDE-ALUMINATE SPECIATION IN ALKALINE  
RADIOACTIVE WASTE

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## Actinide-aluminate Speciation in Alkaline Radioactive Waste

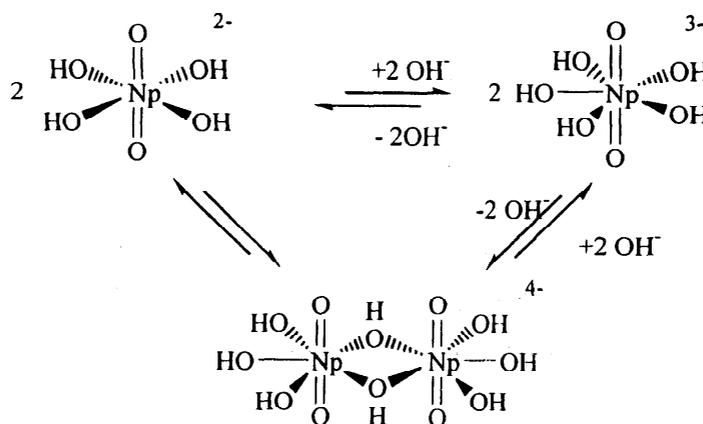
David L. Clark

**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, aluminate [ $\text{Al(OH)}_4^-$ ] 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 (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, etc. It is already known, 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 have only been determined during this program. We are continuing to characterize high-valent TRU elements bound to oxo, water,  $\text{OH}^-$ , under waste-like and sludge washing conditions. These 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 mols/kg. Molecular structure-specific probes include vibrational (IR and 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 the knowledge gained during this project will impact on clean-up approaches to significantly reduce costs, schedules, and risks.

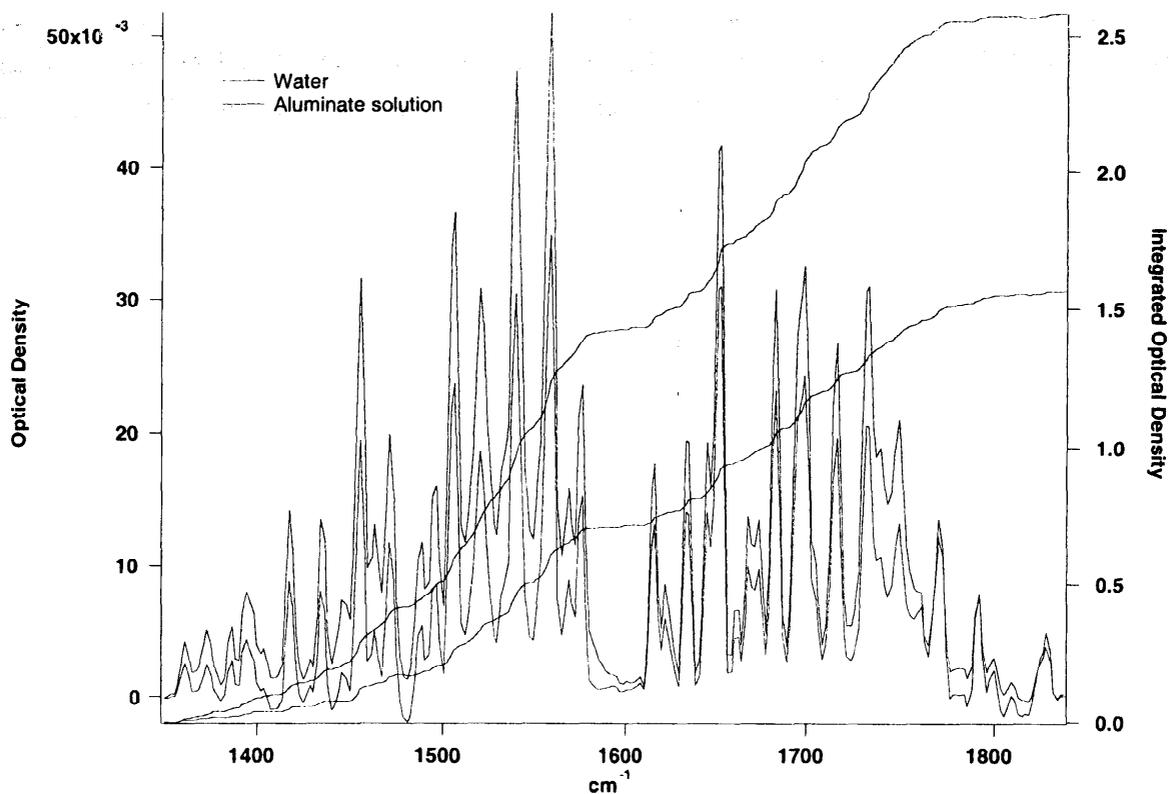
### Research Progress and Implications:

In the first two 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. During our studies of uranium speciation in the presence of aluminate anions under alkaline, waste tank-like conditions (3.5 M (TMA)OH / 0.5 – 1 M  $\text{Al(OH)}_4^-$ ), we discovered a new uranium species. The utilization of (TMA)OH is necessary due to the formation of insoluble uranates in the presence of alkali metal cations. Despite our original hypotheses that an actinide-aluminate coordination complex was formed, our more detailed studies have shown that the aluminate anion is not found in the metal coordination sphere. Rather, we have identified a complex equilibrium involving monomeric and multimeric species as shown in Scheme 1. A similar equilibrium has now also been observed with the Np(VI) system in aluminum-containing NaOH solutions, where the equilibria are significantly shifted to the monomeric side of Scheme 1 in the presence of aluminate. The scheme shows a dimer, however, we still cannot rule out species with a higher nuclearity.



**Scheme 1**

The data indicate that the aluminate acts as an electrolyte, and increases the hydroxide ion activity and hence the overall solubility via formation of  $\text{AnO}_2(\text{OH})_5^{3-}$  ( $\text{An} = \text{U}, \text{Np}$ ). This year we have tested this hypothesis by directly studying the effect of aluminate on the solution thermodynamics. We have used vapor phase IR spectroscopy to indirectly detect the effective concentration of water in solution. This, in turn, we expect to be directly related to hydroxide ion activity. Figure 1 shows that the basic aluminate solutions exhibit much less water vaporization than a pure water sample does. This is in accord with the microscopic viewpoint that the solutes 'tie up' solvent molecules, in this case water in association with aluminate and hydroxide ionic species. This hypothesis must be verified by developing van't Hoff data (intensity vs.  $T^{-1}$ ) to check for changes in the enthalpy of vaporization of water from the



**Figure 1:** A comparison of water vapor infrared absorbance over a solution of deionized water and a solution containing 0.6 M aluminate in 4M NaOH (both solutions are at 21 °C and with a 4 cm pathlength at ambient pressure).

different solutions. If none are detected, then it will be reasonable to correlate the vapor phase signal inversely with the solute effective concentrations. These effective concentrations (activities) are expected to be much more predictive of solution chemistry.

We have also studied the behavior of plutonium under these waste-tank and sludge-washing conditions. For Pu, the presence of carbonate in the alkaline solutions derived from atmospheric CO<sub>2</sub> gives an even more complex set of species. Data have been obtained indicating the presence of not only hydroxo complexes but also carbonato complexes up to the tris-carbonato end-member, PuO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>. This contrasts the behavior of both uranium and neptunium, neither of which form significant carbonato species under these conditions.

These data 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 equilibria discussed above. Each of the light actinides have been found to behave differently, whether it be uranium which precipitates to form uranates, neptunium which forms soluble hydroxo complexes, or plutonium which forms both hydroxo and carbonato complexes. These data only further demonstrate the need to do experiments on each of the actinides as opposed to just surrogate experiments on a single element to model expected chemistry.

**Planned Activities:** The experiments discussed above have opened a number of new research avenues. In the final one half year we plan to finalize the work on the effect of aluminate on solution thermodynamics of hydroxide and now also carbonate. In order to accomplish this goal we will continue to use the wealth of spectroscopic tools at our disposal, including vibrational (IR, Raman), NMR, electronic spectroscopies, etc. We will also be preparing a number of publications detailing the scientific progress of the last two and one half years to ensure the transfer of the technological data to the technical planners at the DOE sites.

**Information Access:** A manuscript describing the spectroscopic data leading to the description of Scheme 1 above is in the process of being submitted for publication and another publication detailing the effect of aluminate on water and hydroxide activity will be submitted in the fall.