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Title: ACTINATE-ALUMINATE SPECIATION IN ALKALINE
RADIOACTIVE WASTE

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Actinide-aluminate Speciation in Alkaline Radioactive Waste Mid-Year Progress Report

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Goals of Project:

The results of this proposed research will contribute fundamental new knowledge on structural and thermodynamic data of actinide-aluminate complexes that may be applied directly to identification and characterization of radionuclide-aluminate complexes in the tanks that can mobilize the actinides and thereby affect the design of treatment methods for actinide-containing tanks. 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 anticipate that such new knowledge will impact on clean-up approaches to significantly reduce costs, schedules, and risks.

Technical Description of Work:

- Determination of TRU (Np, Pu, Am) speciation with aluminate anions under alkaline, oxidizing waste-like conditions. 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, $AnO_2(OH)_n^{2-n}$. The presence of aluminate ions causes the solubilities to increase, although the exact species are not known.
- Characterization and stability of high-valent TRU's bound to oxo, water, OH^- , $Al(OH)_4^-$, and AlO_2^- 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.
- Use of structure-specific probes that we have successfully employed for TRU speciation in alkaline conditions, Pu processing, Yucca Mt. tuff, and WIPP brine studies. They are Raman, multinuclear nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS), luminescence, optical absorption (UV-Vis-conventional and photoacoustic) spectroscopies.
- Results of study will provide data for the next generation of separations, thermodynamic modeling, and risk assessment.
- Characterization of TRU adsorption / coprecipitation to aluminate solids (boehmite, gibbsite) present in waste tanks in order to assess the treatability and radionuclide separation scheme of sludges and waste streams.

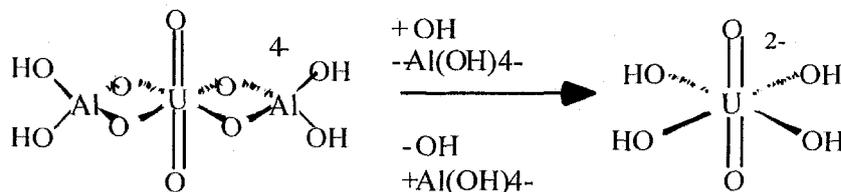
Accomplishments to Date:

In the eight months since the inception of this program, significant progress has been made in understanding the behavior of aluminates and actinide elements under highly alkaline conditions. The initial efforts in this research have focused on an evaluation of the conditions under which aluminate ions interact with U(VI). Solubility studies were performed to determine the stability field of U(VI) under highly alkaline conditions (2.5 – 3.5 M OH⁻) in the presence of aluminates. Under a different program we had determined that U(VI) solubility is extremely low in alkali metal hydroxide solutions (eg. LiOH, NaOH, KOH, and CsOH), giving rise to the formation of uranates. Through the utilization of a bulky alkyl ammonium cation, tetramethyl ammonium (TMA), the solubility of uranium was raised significantly (~ 0.1 M). Similar behavior was also observed in our studies of aluminate solutions. The presence of alkali metal cations in the aluminate solutions leads to the formation highly insoluble species; however the use of (TMA)OH as the base allowed for solutions with uranium concentrations as high as 0.1M. It should be noted that for Np and Pu, alkali metal hydroxide solutions are not so dilute in actinide concentration. The use of TMAOH allows us to use uranyl as an initial surrogate for these radionuclides for the initial scoping experiments.

With the physicochemical properties determined for U(VI), a multi-disciplinary approach to understand the uranyl, UO₂²⁺, complexation within these solutions was undertaken. The techniques utilized include, electrochemistry, absorption, emission, and vibrational spectroscopy, extended X-ray absorption fine structure (EXAFS), nuclear magnetic resonance (NMR), and single crystal X-ray diffraction. The absorption and emission spectroscopy were studied first, since these techniques could most easily identify changes in the coordination sphere of the uranium atom. Our preliminary studies employing luminescence spectroscopy at liquid nitrogen temperature indicates that the spectra and lifetimes change dramatically in the presence of Al(OH)₄⁻ in TMA(OH) solution, indicating that a new solution species is present. We expanded on these experiments by performing systematic studies of the concentration dependence of both uranium and aluminate. The concentration of aluminate was maintained at either 0.5 or 1.0 M with a total [OH⁻] of 3.5 M. The uranium concentration was varied to a much greater degree, ranging from 0.02 – 50 mM. The seemingly simplest system is the one with 1.0 M Al(OH)₄⁻. The luminescence spectra at uranium concentrations from 0.02 – 20 mM show a typical uranyl emission starting at ~ 21,500 cm⁻¹ with five well resolved lines, resulting from the vibronic coupling to the linear dioxo unit. First analysis of this data would indicate that a single species was present in the frozen solution. However, a small red shift in the spectra is observed as the uranium concentration increases, indicating the presence of another minor species. At 50 mM U(VI) the spectrum is significantly different in that there are clearly two progressions originating from two species. Further data for the presence of two species was obtained by performing a gated emission experiment. In this study, the sample was pulsed and the data collection was initiated after a 50 μs delay. The resulting spectrum left a single broad peak, which was red-shifted (~ 18,500 cm⁻¹) with respect to the original clearly resolved progression. The resulting spectrum was compared to an alkaline solution (3.5 M (TMA)OH) of U(VI) in the absence of any

aluminates. In this system it is known that an equilibrium exists between two species, $\text{UO}_2(\text{OH})_x^{2-x}$ ($x = 4, 5$), where the pentahydroxide shows a spectrum at $\sim 21,000 \text{ cm}^{-1}$ with a well resolved vibronic coupling while the tetrahydroxide shows a single broad peak at $\sim 18,500 \text{ cm}^{-1}$. The comparison of the aluminate containing spectra and the aluminate-free spectrum suggests that an equilibrium system is present where aluminate can act as a ligand to the uranium. Equation 1 gives one proposed equilibrium, but it should be noted that a number of equilibria could be conceived to explain the current data.

Equation 1.



In order to pursue this equilibrium further, the uranium concentration was increased again to 100 mM U(VI). This solution gave a spectrum almost identical to that of the non-aluminum containing alkaline solution, indicating that at high U:Al ratios the equilibrium shown above is shifted to the right.

Results from the 0.5 M $\text{Al}(\text{OH})_4^-$ solutions gave similar results as the 1.0 M aluminate solutions. For these experiments the uranium concentrations were also varied from 0.02 to 50 mM U(VI). What was most striking in this study was the rate at which the emission spectra showed the formation of the "pure" hydroxo complexes. At 0.02 mM U(VI) the spectrum resembled that of the 1.0 M aluminate, a well resolved blue shifted spectrum. However, in the 0.5 M aluminate solutions by the time the U(VI) concentration was raised to 20 mM conversion into the $\text{UO}_2(\text{OH})_x^{2-x}$ ($x = 4, 5$) system was already significant. For the 1.0 M aluminate, much larger concentrations of uranium were required before aluminate complexation lessened.

With the emission data giving the solution conditions under which single species are most likely present, subsequent characterization methods were employed, eg. electrochemical, EXAFS and vibrational. The electrochemistry was performed at 10 mM U(VI) and 0.5 or 1.0 M $\text{Al}(\text{OH})_4^-$. Under these conditions the 1.0 M aluminate solution had mostly the aluminate complex present, whereas the 0.5 M aluminate solution contained a distinct mixture of species. Both solutions showed quasi-reversible behavior, indicating significant stability of the penta-valent state of uranium. The reduction potentials for both solutions were found to be more negative than the non-aluminum containing alkaline solutions. The $E_{1/2}$ values for the 0 M, 0.5 M, and 1.0 M $\text{Al}(\text{OH})_4^-$ solutions are as follows -0.92 , -0.95 , and -0.96 V , respectively. The kinetics of the reduction were also studied and found to vary with the aluminate concentration. Another piece of evidence, which indicates the presence of aluminate complexation was the diffusion rates. Diffusion rates are essentially the rate at which a species diffuses to an electrode. The larger the species generally the slower the diffusion. It was found that the slowest diffusion rates were observed with the 1.0 M aluminate solutions by almost a factor of 4 compared to the non-aluminum containing solution. This phenomenon can be explained by the presence of aluminate ligands on the uranyl center,

thereby increasing the size and molecular weight of the complex. The shift in the $E_{1/2}$ values can also be justified by aluminate complexation followed by deprotonation of the aluminate ligand as shown in equation 1. The effect of the deprotonation is an increase in the negative charge on the complex making it slightly harder to reduce.

In the course of obtaining vibrational data on possible uranyl-aluminate-hydroxo species, we often obtained a precipitate consisting of the uranyl, nitrate, and aluminate. The symmetric uranyl stretch, as determined by Raman spectroscopy, increased in frequency as the uranyl/aluminate ratio was increased. This systematic change indicates a bonding interaction in the solid due to the presence of aluminate, with implications of the form of the TRU in sludges and precipitates in tanks. A similar shift was not observed in the supernatant. However, in aged samples, which were allowed to sit open to the atmosphere, the supernatant has been observed to go from a uranyl-hydroxo species to a uranyl tris-carbonato species. The result was confirmed by both vibrational spectroscopy and a single crystal XRD study of $(TMA)_4UO_2(CO_3)_3 \cdot 3H_2O$. This result is not that surprising in that highly alkaline solutions collect vast amounts of carbonate by adsorbing CO_2 from the air, where CO_2 (aq) is a weak acid, which subsequently reacts with base to form carbonate. The formation of the tris-carbonato TRU species and the subsequent high solubility, indicate the importance of including these species within the sludge washing separation scheme.

Finally, an EXAFS analysis was performed on two solutions of U(VI) in 0.5 and 1.0 M aluminate. The concentration of uranium in both solutions was approximately 0.1 M. Under these conditions the emission data would predict that the major species should be the penta-hydroxo complex. The analysis of the EXAFS of these solutions confirmed this hypothesis. The fourier transform of the data showed a single asymmetric peak, identical to that obtained from solutions not containing aluminum. In addition, the solutions did not show any aluminum shell which may have been expected if a bridging or monodentate aluminate ligand was present.

The preliminary conclusions from these studies was the essential element within this system appears to be the ratio of U:Al, where large ratios lead to the formation hydroxo complexes and low ratios lead to aluminate complexation. With this data in hand further studies using NMR, EXAFS, and vibrational work may continue.

Projections:

The workscope for this year was altered in order to proceed with an increased efficiency. A decision was made to limit this first year's studies to uranium. This process has allowed us to begin mapping out a complex chemistry with a metal center having the most spectroscopic tags. Therefore, the originally planned plutonium work will be postponed to the next FY. The uranium scope will be completed and expanded. The remaining work for this year will focus on additional spectroscopic analysis to understand the complexes present. 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}O - and ^{27}Al -NMR will be performed to studying the nature and thermodynamics of the equilibrium.

Funding:

The budget for this project is following along initial projections. Currently ~\$200K of the \$380K allocation has been spent. The projections for the remainder of this FY are linear and it is expected to be at \$0K by the end of September. At this time the project is expected to be accomplished within the budget.

Issues/Problems:

The main difficulties within this project have been the allocations of the money to the laboratory. Initially, the full allocation of \$380K was not going to be distributed to LANL. This has been rectified earlier this year. Another funding difficulty was the distribution of the funds for the Russian collaborators involved with this project. The funds never made it to the Russian Academy of Sciences. To the best of our knowledge the hold-up was at DOE and this is currently being resolved.

Corrective Actions:

N/A

Additional Information:

Progress Tracking Systems
Environmental Management Science Program Report
Technical Task Plan #AL18SP24

April, 1999

Significant Problems/Issues/Concerns:

N/A

Corrective Actions:

N/A

Summary Assessment:

We have initiated scoping experiments, and will focus on aluminate complexation of uranium in the first year.

Cost Variance:

N/A

Schedule Variance:

On Schedule

Technical Status:

In the course of obtaining vibrational data on possible uranyl-aluminate-hydroxo species, we often obtained a precipitate consisting of the uranyl, nitrate, and aluminate. The symmetric uranyl stretch, as determined by Raman spectroscopy, increased in frequency as the uranyl/aluminate ratio was increased. This systematic change indicates a bonding interaction in the solid due to the presence of aluminate, with implications of the form of the TRU in sludges and precipitates in tanks. However, in aged samples, which were allowed to sit open to the atmosphere, the supernatant has been observed to go from a uranyl-hydroxo species to a uranyl tris-carbonato species. The result was confirmed by both vibrational spectroscopy and a single crystal XRD study of $(TMA)_4UO_2(CO_3)_3 \cdot 3H_2O$.

Major Accomplishments:

- Obtained supporting data consistent with formation of aluminate complexation.
- Obtained preliminary data detailing the importance of CO_3^{2-} complexation in aging solutions.