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Recent Studies of Uranium and Plutonium Chemistry in Alkaline Radioactive Waste Solutions

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ABSTRACT

Solubility studies of uranium and plutonium in a caustic, radioactive Savannah River Site tank waste solution revealed the existence of uranium supersaturation in the as-received sample. Comparison of the results to predictions generated from previously published models for solubility in these waste types revealed that the U model poorly predicts solubility while Pu model predictions are quite consistent with experimental observations. Separate studies using simulated Savannah River Site evaporator feed solution revealed that the known formation of sodium aluminosilicate solids in waste evaporators can promote rapid precipitation of uranium from supersaturated solutions.

Keywords: A. actinide alloys and compounds, B. precipitation, D. x-ray diffraction

INTRODUCTION

Historical operations of United States Department of Energy facilities at the Savannah River Site (SRS) in Aiken, SC have generated millions of gallons of highly radioactive wastes that are stored in large underground storage tanks comprised of carbon steel. The highly alkaline wastes within the tanks consist of three forms: sludge, supernate, and saltcake. Sludge solids were produced when acidic wastes from the purification of irradiated nuclear fuels and targets were neutralized and consist of transition metal hydroxides and oxy-hydroxides along with similar compounds of aluminum. Aqueous supernate solutions contain the soluble components of the neutralized fuel reprocessing solutions and are largely a mixture of dissolved salts, predominantly sodium hydroxide, sodium nitrate and sodium nitrite. Saltcake solids were formed by evaporation of the supernate during storage within the tanks and are largely sodium salts of nitrate and nitrite. Small quantities of uranium and plutonium are partitioned in the tanks within these three waste types.

Retrieval of sludge solids from the storage tanks began in the 1990's and sludge is currently being vitrified at the SRS Defense Waste Processing Facility (DWPF) in a borosilicate glass matrix for disposal in the federal repository for High-Level Waste. The alpha component of the other two waste classes (supernate and saltcake) must be reduced prior to shallow land burial of these materials at SRS. The alpha removal technology is a batch contact method with monosodium titanate sorbent and has been well tested [1]. The waste processing strategy calls for the saltcake to be dissolved with water and batched through the alpha removal process along with the supernate wastes. These operations will require numerous waste transfers and result in the mixing of many waste streams.

The chemistry of uranium and plutonium is of interest in these processing steps to ensure that their concentrations due not exceed solubility limits, resulting in the precipitation of actinides or the occlusion or sorption of actinides with other solids formed. Even though the actinide concentrations are generally low in waste supernate solutions, the large volumes involved (millions of gallons) can lead to criticality concerns associated with fissile material deposition in these solid forms. The solubilities of actinides under caustic conditions has been previously studied. Allard compiled, measured, and estimated complex formation quotients for the actinides as a function of oxidation state in the pH range 7 to 11 [2]. Delegard studied the solubility of plutonium (IV) hydrous oxide in synthetic Hanford Site high-level waste solutions [3]. Hobbs and Karraker measured uranium and plutonium solubilities in simulated SRS waste solutions and developed solubility models as a linear function of a number of anion concentrations and temperature [4]. In addition to promoting actinide precipitation, the mixing of various process solutions and the concentration of supernate solutions in evaporators (a common SRS tank farm management practice) can result in the precipitation of other compounds like aluminosilicates, which have been shown to occlude actinides [5]. As a result of these concerns, tests have been conducted at the Savannah River National Laboratory (SRNL) to determine the solubility of these elements in various types of actual waste solutions and to examine the chemistry of uranium and plutonium under potential process scenarios.

EXPERIMENTAL DETAILS

A supernate sample was retrieved from an SRS waste tank containing DWPF recycle solution. Sample characterization revealed that the primary waste components were 0.49 M Na^+, 0.17 M free OH^-, 0.05 M NO_3^-, and 0.16 M NO_2^-. Carbonate analysis results indicated that the concentration was <0.3 M. The sample also contained numerous other minor components present at concentrations • 5 E-2 M. U and Pu concentrations in the as-received sample were 19 and 3.8 E-04 mg/L, respectively. U and Pu solubility tests were conducted by two methods. Acid spike tests involved sequential addition of small volumes (<2 volume % total dilution) of uranyl nitrate and plutonium oxide solutions to give theoretical U and Pu concentrations of 2400 and 28 mg/L, respectively. Solids addition tests were conducted by spiking fresh supernate samples as described above and isolating the solids after 24-48 hours on 0.45 micron filters. The solids were immediately washed with additional small volumes of fresh supernate, and then transferred to yet another sample of fresh supernate which was half of the volume of the original spiked sample. As a result, the exact mass of solids added is unknown but is believed to greatly exceed the solubility of U and Pu in this supernate. All samples were placed in an orbital shaker oven at 27 ºC and agitated at 240 RPM for • 20 days. Solution sub-samples were periodically analyzed for uranium and plutonium after filtration through 0.45 µm syringe filters and acidification in nitric acid. Tests were continued until equilibrium was established based on the analysis results obtained for samples collected over a period of several days.

Testing was also conducted using a simplified waste simulant to evaluate uranium deposition under conditions promoting sodium aluminosilicate precipitation. A simulant was prepared containing 4.0 M NaOH, 1.0 M $NaNO_3$, 1.0 M $NaNO_2$, 1.7 E-3 M SiO_2 and 1.7 E-2 M Al (III). This simulant composition is typical of SRS waste evaporator feed solutions. The solution was heated to 50 ºC and uranyl nitrate was added to give a U concentration near 60 mg/L, which was believed to be well above the solubility limit for uranium. The solution was spiked to give a final Al concentration near 2 g/L, filtered, and held at 50 ºC for approximately 2 days. The sample was then spiked with sodium metasilicate at 50 ºC to give a final silicone concentration near 1 g/L. These conditions are known to promote aluminosilicate formation. The solution concentrations of Si, Al, and U were monitored over the next 10 days by periodically analyzing solution sub-samples isolated by filtration through 0.45 µm Nylon filters and acidified in nitric acid.

RESULTS AND DISCUSSION

Uranium and plutonium solubilities in the actual DWPF recycle sample were measured using a technique modified from that used by Addai-Mensah, et. al. [5]. The method includes both the spiking of supernate solutions with small volumes of acidic uranyl nitrate and plutonium oxide solutions (acid spike), and the direct addition of preformed uranium and plutonium solids to fresh supernate (solids addition). Solubility data for U and Pu obtained by both of the above described methods are provided in Figure 1 along with solubility predictions and confidence intervals generated using the statistical models developed by Hobbs, et. al. [4]. The statistical model for uranium solubility does not accurately predict the solubility for this waste composition. The predicted U solubility limit of 51 mg/L was ~6 times greater than the average observed solubility (8.3 mg U/L) and all observed values were well outside the 95% confidence intervals for the model. Obviously, further model refinements will be required in order to accurately predict uranium solubility for actual supernate samples across the range of waste compositions. Furthermore, it appears that the as-received DWPF recycle sample was supersaturated in uranium, since the initial measured uranium concentration was 19 mg/L. Uranium supersaturation has been observed over extended time periods in tank waste supernates during other SRNL testing. The fact that supersaturated solutions may already exist in the SRS tank farm increases the likelihood that unexpected precipitation of uranium could occur during waste processing.

The as-received DWPF recycle sample was not supersaturated in plutonium (initial [Pu]: 3.8 µg/L). The plutonium solubilities determined by the two test methods were similar (acid addition – 5.8 µg/L; solids dissolution – 8.0 µg/L) and were near the predicted value of 4.7 µg Pu/L. Solubility test results for several other tank supernate samples (to be reported separately) reveal that Pu solubility is typically • 5 mg/L, while U solubility limits can approach 50 mg/L. The solubilities vary with the concentrations of the primary anions in solution and the temperature.

Characterization of the solids formed during solubility testing with the DWPF recycle sample by x-ray diffraction (XRD) revealed that the primary crystalline solid phase was clarkeite, $Na(UO_2)(OH)O\cdot H_2O$, the hydrated monosodium salt of uranyl hydroxide. A plutonium phase was not observed by XRD due to the relatively small mass of Pu solids formed. Previous studies have indicated that the plutonium solid phase formed under these conditions is $PuO_2\cdot xH_2O$ [3].

The chemistry of uranium was also examined under conditions promoting sodium aluminosilicate formation. Sodium aluminosilicate solids have been observed in SRS waste evaporators. In this study, conditions were manipulated to determine the fate of uranium in a supersaturated solution during the formation of aluminosilicate solids. In these experiments, uranium was spiked into the waste solution to near 60 mg/L and held at temperature (50 °C) for 50h. Analysis samples were collected very shortly after uranium addition and at 50 h to determine if the uranium had precipitated. U, Al, and Si analysis results are provided in Figure 2. An aliquot of sodium metasilicate was added to the waste solution to increase the Si concentration to near 1 g/L. Additional analysis samples were collected immediately following the metasilicate addition and periodically over approximately 200 h. During the 50th hour, just after metasilicate addition, simultaneous reductions in the aluminum and silicon concentrations were observed, indicating that the formation of aluminosilicate solid phases had commenced. The formation of alumuminosilicate solids was accompanied by a rapid decrease in the uranium concentration to near 18 mg/L. As is evident from the gradual decrease in both aluminum and silicone concentrations, aluminosilicate formation continued over the duration of the test. In contrast, the uranium concentration was relative stable during the remainder of the test. These observations are consistent with rapid removal of uranium from a supersaturated solution promoted by the presence of aluminosilicate solids. The final uranium concentration of 18 mg/L presumably represents the solubility limit for uranium at 50 ºC for this waste composition.

CONCLUSIONS

The successful processing of SRS high-level waste requires an understanding of the fate of uranium and plutonium under prototypical processing scenarios. These studies have shown that certain existing SRS tank supernates are supersaturated in actinides (specifically U in this case) and have identified a known SRS process phenomenon (aluminosilicate formation in waste evaporators) promoting the rapid precipitation of U from supersaturated solutions. Results of these studies will assist SRS engineering personnel in the development of schemes and sequences for the retrieval and processing of the stored waste solutions at the Savannah River Site with minimal deposition of actinide solids.

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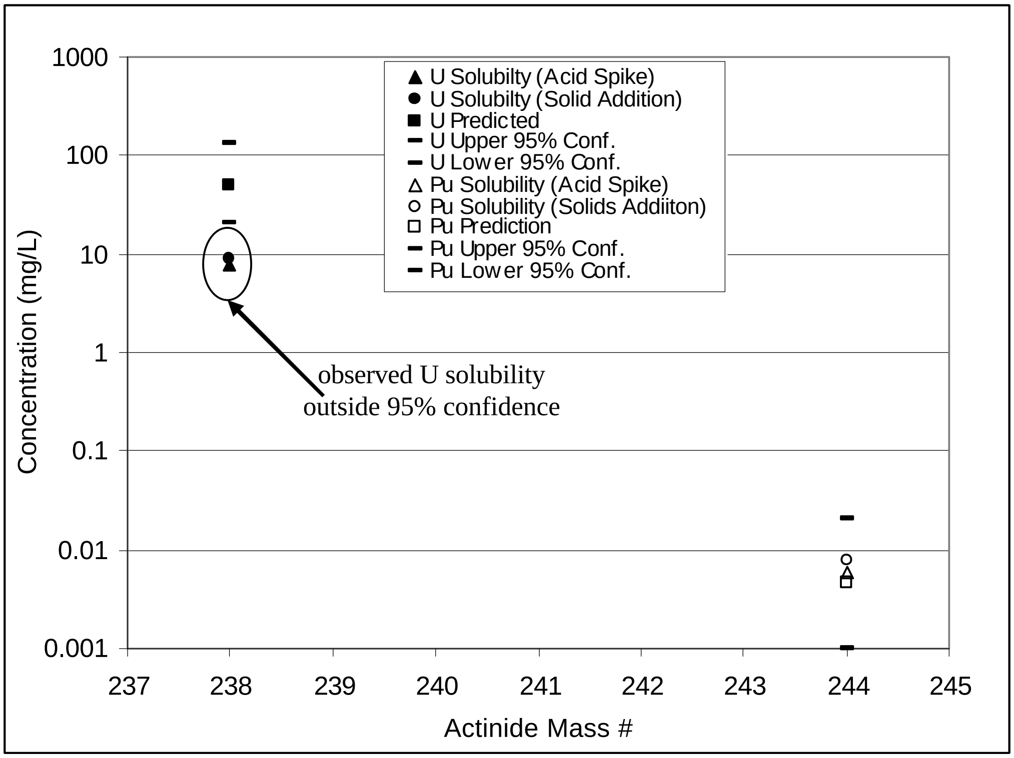

Figure 1. Measured and Predicted U and Pu solubilities in Actual SRS DWPF Recycle.

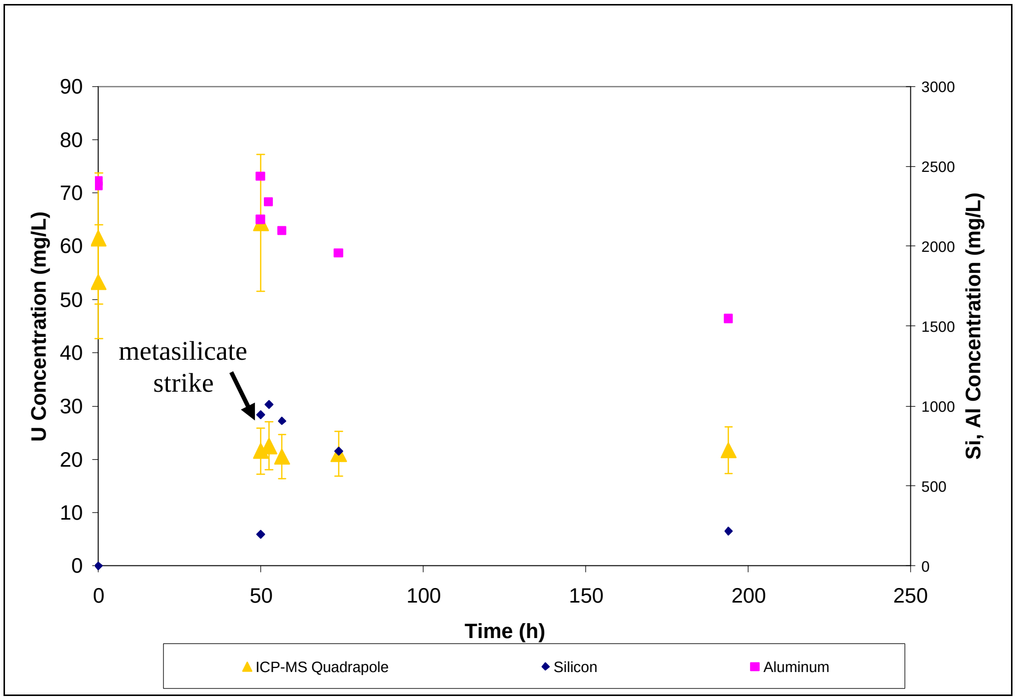

Figure 2. U, Si, and Al Concentrations during Aluminosilicate Formation at 50 ºC in Simulated SRS Evaporator Feed.