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Purification of Uranium from Uranium/Molybdenum Alloy

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ABSTRACT

The Savannah River Site will recycle a nuclear fuel comprised of 90% uranium-10% molybdenum by weight. The process flowsheet calls for dissolution of the material in nitric acid to a uranium concentration of 15-20 g/L without the formation of precipitates. The dissolution will be followed by separation of uranium from molybdenum using solvent extraction with 7.5% tributylphosphate in n-paraffin. Testing with the fuel validated dissolution and solubility data reported in the literature. Batch distribution coefficient measurements were performed for the extraction, strip and wash stages with particular focus on the distribution of molybdenum.

uranium
molybdenum
solubility
distribution
solvent extraction

INTRODUCTION

The Super Kukla (SK) Prompt Burst Reactor operated at the Nevada Test Site from 1964 to 1978. Typical SK material is 90% uranium (U)-10% molybdenum (Mo) by weight at approximately 20% ^{235}U enrichment. The material consists of annular rings, disks, and rods where the rings and disks have a 0.005-inch nickel (Ni) plating. The SK material is being considered for dissolution in the Savannah River Site (SRS) H-Canyon facility and the solution containing the dissolved material will be used as aqueous feed for the PUREX solvent extraction process for U recovery. The recovered U must contain less than 800 μg/g U to meet the requirements for the SRS high enriched U blend-down program.

Solubility

Solubility data for the dissolution of molybdic oxide (MoO_3) in solutions of U and nitric (HNO_3) were reported by Faugeras, et al. as a function of U and HNO_3 concentrations.(1) The solubility of Mo as MoO_3, molybdic oxide dihydrate ($MoO_3 \cdot 2H_2O$), or MoO_4^{2-} in HNO_3 solutions in the presence of UO_2^{2+} and/or Fe^{3+} has been reported by Ferris.(2) Both MoO_3 and $MoO_3 \cdot 2H_2O$ are sparingly soluble in HNO_3; maximum MoO_3 solubility is 0.05M at 3M HNO_3 and $MoO_3 \cdot 2H_2O$ has maximum solubility of 0.13 M at 3.5 M HNO_3. Mo solubility from UO_2MoO_4 is maximized at 0.18 M Mo at 3 M HNO_3.(2)

Although the solubility of Mo in acidic solutions is low, it was sufficient for Piqua fuel processing (97% U-3% Mo) at the Savannah River Site (SRS). At 100 °C, the maximum solubility of Piqua fuel was approximately 100 g/L U and 4 g/L Mo in 2-3 M HNO_3.(3) The best data available for evaluating the solubility of dissolved SK material in HNO_3 at ~20 g/L U is a linear interpolation of the data of Faugeras.(1) The experiments discussed here were conducted to validate the interpolation at the targeted SRS operating condition of ~20 g/L U.

Solvent Extraction

The PUREX process is well-known as a solvent extraction method for separating actinides from aqueous matrices that contain a variety of dissolved metal cations and fission products. Elements such as aluminum, iron, and nickel, which are frequently present in fuel as bonding or cladding agents, are not extracted by TBP. The SK fuel contains Ni cladding which, after dissolution, would remain in the aqueous phase during solvent extraction.(4) With TBP, Mo distribution ratios with or without U suggest Mo would also remain in the aqueous phase.(5)

Occasionally, aqueous solvent extraction feed composition is such that species that normally are not extracted are present in the organic phase. Previous SRS solvent extraction results with U-Mo fuels showed Mo distribution coefficients greater than one, indicating some Mo is present in the organic phase.(3),(6) However, under conditions that maximize Mo extraction, adequate U recovery and Mo separation were observed after processing through the extraction, scrub, and strip stages of solvent extraction. During these tests, most of the Mo was rejected to the aqueous waste and less than 10ppm Mo was detected in the U product. (7) The SRS H Canyon facility requested batch solvent extraction studies with the SK material to verify Mo decontamination.

EXPERIMENTAL

Chemicals

The SK material was obtained from Oak Ridge and was reported to contain 90% U (20.1% ^{235}U) and 10% Mo by weight. Nitric acid (68.7 wt. % assay) and $Fe(NO_3)_3$-$9H_2O$ (98.4 wt. % assay were purchased from Fisher Scientific Tributylphosphate was received from Acros and n-paraffin from H Canyon supplies. All chemicals were used as received.

Solubility

Three different starting HNO_3 concentrations were used: 4 M, 5 M, and 6 M. The starting acid solutions also contained 1 g/L of ferric ion (Fe^{3+}) added as ferric nitrate hydrate [$Fe(NO_3)_3 \cdot 9H_2O$]. The iron in solution simulates iron from dissolved carbon steel cans and charge bundle hardware. The test vessel was a 1-liter borosilicate glass unit with a cover that contained penetrations for a thermocouple, check valve, and sample basket holder. The vessel was placed on a hot plate with solution temperature and stirring control capabilities.

The SK material was dissolved in 500 mL of HNO_3. The acid in the test vessel was heated to temperature (either ~70 °C or ~100 °C). Temperature was measured using a Type K thermocouple. At the beginning of each test, the SK sample was placed into a sample basket and suspended above the acid. Dissolution tests were performed by lowering the basket containing the sample into the acid for a specific amount of time and pulling the sample out of the dissolver. The undissolved sample was then rinsed with deionized water, dried, weighed, and physical dimensions measured. Mass was measured using a calibrated balance accurate to 0.001 g. The physical dimensions of the SK sample are not reported as part of this study.

The volume of liquid inside the dissolving vessel was occasionally measured using a 1-liter graduated cylinder to account for volume losses due to acid consumption and evaporation. Aliquots of the solution containing increasing amounts of dissolved SK material were set aside for analysis by inductively coupled plasma mass spectroscopy (ICPMS), inductively coupled plasma emission spectroscopy (ICPES), free acid by titration, and gamma spectroscopy. Larger aliquots from dissolution tests were collected and used in subsequent testing (Table 1). The samples were allowed to set for 21 days at room temperature for observations.

Table 1. Test Solution Aliquots for Follow-up Dissolution Studies

Start HNO_3 (M)	**T (°C)**	**SK (g/L)[#]**	**Volume (mL)**	**Start HNO_3 (M)**	**T (°C)**	**SK (g/L)[#]**	**Volume (mL)**
4	100	35.6	100	5	70	33.3*	258
4	70	46.1*	315	6	100	14.0	100
5	100	22.3	100	6	70	20.6*	100
5	70	28.4*	100	6	70	24.3*	255

* Fine brown precipitate observed in solution

[#] Based on SK sample weight change and solution volume

U-Mo Batch Distribution Coefficients

Two aqueous solutions containing U and Mo were prepared as solvent extraction feed by diluting solutions produced from the SK solubility experiments. First, an appropriate volume of solution containing 35.5 g/L (U + Mo) in nominally 4 M HNO_3 was transferred into a 50 mL graduated cylinder followed by addition of 4.5 M HNO_3 to produce a solution containing, nominally, 20 g/L (U + Mo) in 4.0-4.2 M HNO_3. Second, an appropriate volume of solution containing 33.3 g/L (U + Mo) in nominally 5 M HNO_3 was transferred into a 50 mL graduated cylinder followed by addition of 5.5 M HNO_3 to produce a solution containing, nominally, 20 g/L (U + Mo) in 5-5.2 M HNO_3.

These experiments were performed in duplicate. All solutions were added, removed, or transferred using adjustable volume pipettes. Intimate mixing of the aqueous and organic phases was performed using a vortex mixer for 30 seconds. The distribution coefficients are reported as the concentration of the element in the organic divided by the concentration of the element in the aqueous phase. A detailed description of the volumes and the process followed during the solvent extraction experiments is available elsewhere.(4)

RESULTS AND DISCUSSION

Solubility

Dissolution of the SK material in 4-6 M HNO_3 at 70-100 ^{o}C progressed with vigorous bubbling and release of nitrogen oxide (NO) and nitrogen dioxide (NO_2) gases. NO_2, an orange-brown gas, was present in the vessel head space. The presence of NO, which is colorless, was inferred based on a more intense orange-brown color when the vessel head space gas was allowed to react with air; NO reacts with oxygen (O_2) in the air to form NO_2.

It is worth noting that the SK material initially contained Ni plating, which dissolved readily. Nickel will comprise less than 0.5% of the total mass of the actual SK material. Nickel dissolved readily into the first sample (4 M HNO_3 and 35.6 g/L U+Mo), remained at the same concentration for the second sample (4 M HNO_3 and 45 g/L U+Mo), and was totally absent from all subsequent tests which used fresh starting solutions. The Ni dissolution behavior is consistent with Piqua fuel dissolution, which contained 0.5 wt% Ni. The Ni in the Piqua fuel readily dissolved into HNO_3 and did not yield a precipitate.(3)

It was observed that the dissolutions at 100 ^{o}C were successful in maintaining the solution conditions below the solubility limit for the SK material. However, when additional dissolutions were performed at ~70 ^{o}C, reddish-brown precipitates were observed. Liquid samples were filtered and submitted for analysis by ICPES, gamma spectroscopy and free acid by titration. The data are contained in Table 2. The total U data as measured by gamma and ICPES show good agreement, although notably lower than the value calculated based on sample weight change. The ICPES data for Fe are all very close to 1 g/L, which is the initial concentration of Fe put in the starting solutions.

The presence of the solids was a byproduct of the experimental method. Each time the sample was removed from solution to obtain a weight, the hot sample reacted with air and formed an oxide coating. When the sample was re-introduced into the solution, the oxide coating detached from the metal surface and did not dissolve readily in HNO_3 below 80 °C. Later experiments, not discussed here, demonstrated that the solids will dissolve above 80 °C.(4)

The color of the oxide coating on the metal sample resembled the color of the solids observed during dissolution. Analysis of the solids using x-ray diffraction was inconclusive. Analysis using scanning electron microscopy (SEM) revealed a non-crystalline solid containing Mo with lesser amounts of Fe and still smaller quantities of U. The relative amounts of Mo, Fe and U could not be quantified from the SEM data, nor can it be determined whether the U is crystalline material or merely present as adsorbed liquid. Schulz has reported an empirical formula for the precipitate of $(UO_2)_3Mo_6O_{21}$, or 42% U and 33 % Mo. Polyions of the formula $(Mo_6O_{21})^{6-}$ have been postulated to exist in acid molybdate solutions.(8)

To evaluate the solubility data for the dissolution of U-10Mo metal alloy against literature data obtained by dissolving MoO_3 in solutions of U and HNO_3, the data of Faugeras were interpolated.(1) To interpolate the data, the data at 0 and 50 g/L U were identified, and then a linear interpolation was performed to arrive at solubility data at 20 g/L U. The interpolated curve for 20 g/L is shown with the 0 and 50 g/L data in Figure 1. Also included in Figure 1 are the ICPES U, ICPES Mo, and free acid data of Table 2, along with the solubility observations made one day after dissolution.

Table 2. ICPES and Gamma Spectroscopy Sample Data

Start HNO_3 (M)	Calc. U-Mo (g/L)	Reflux	Gamma ^{235}U (g/L)	Total U# Based on Gamma (g/L)	ICPES Total U (g/L)	ICPES Mo (g/L)	ICPES Ni (g/L)	ICPES Fe (g/L)	Free Acid (M)
4	35.6	No	5.71	28.4	28.3	3.03	2.35	1.09	3.46
4	46.1	No*	7.65	38.0	37.1	3.75	2.29	1.07	3.42
5	22.3	No	3.46	17.2	18.3	2.11	0	1.03	4.39
5	28.4	No*	4.59	22.8	23.1	2.42	0	1.00	4.39
5	33.3	No*	5.38	26.8	27.0	2.79	0	0.99	4.36
6	14.0	No	2.31	11.5	11.8	1.34	0	1.07	5.40
6	20.6	No*	3.36	16.7	16.7	1.85	0	1.05	5.39
6	24.3	No*	3.90	19.4	19.7	2.15	0	1.07	5.41

* Precipitate present
\# Based on reported ^{235}U enrichment of 20.1%
Data reported with ±10% uncertainty

Recognizing that Mo solubility is a function of U concentration and that the solid line of Figure 1 will move to the left or right depending on the actual U concentration, six of the eight data points plotted in Figure 1 are in clear agreement with the literature data. The data points for 5 M HNO_3 (initial) with 23 g/L U and 6 M HNO_3 (initial) with 17 g/L U are borderline soluble-insoluble. The samples were viewed periodically after dissolution. After 21 days, the two samples that were borderline soluble-insoluble had changed and no longer contained undissolved solids. Unfortunately, analyses of the final solutions were not performed. Overall, the data support the reliability of interpolation of the literature data from MoO_3 dissolution in U and HNO_3 solutions to predict dissolved SK metal alloy solubility at 20 g/L U.

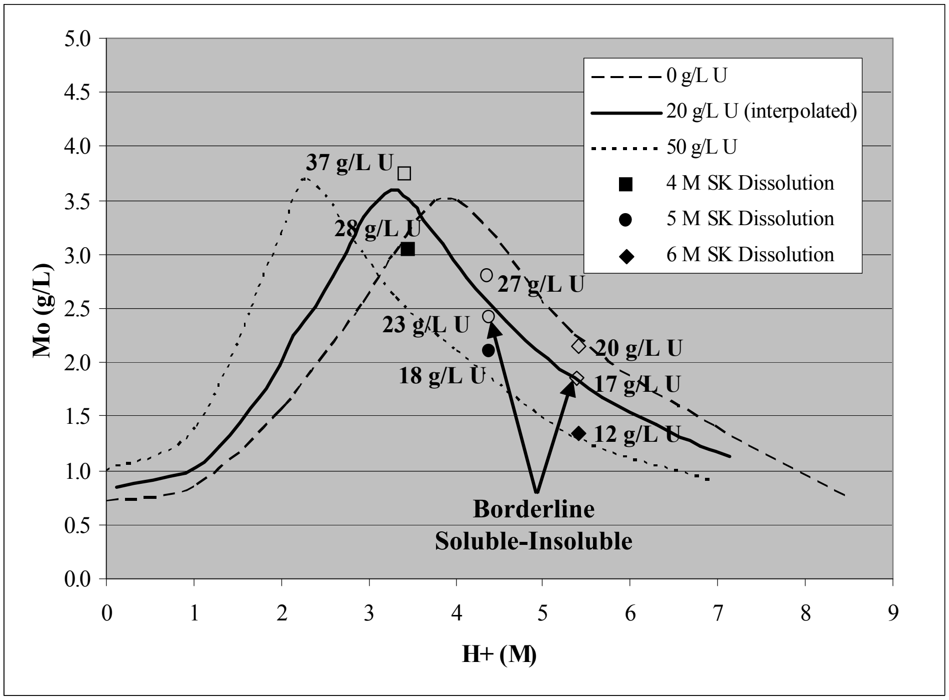

Figure 1. SK Solubility Data vs. Literature Values – One Day after Dissolution (filled symbols indicate no solids; open symbols indicate a precipitate)

U/Mo Batch Distribution Coefficients

The compositions of the aqueous solutions used for solvent extraction feed are summarized in Table 3.

Table 3. Composition of Aqueous Solutions for Batch Solvent Extraction

Initial Solution	^{235}U (g/L)	Total U (g/L)	Mo (g/L)
4 M HNO_3	3.27	16.0	1.73
5 M HNO_3	3.40	15.8	1.83

Data reported with ±10% uncertainty

The SK material contained U with 20% ^{235}U enrichment. Accounting for the ±10% analytical uncertainty, the analysis of both the 4 M HNO_3 and 5 M HNO_3 solutions shown in Table 3 confirmed 20% ^{235}U enrichment in both solutions.

U-Mo Batch Distribution Coefficients: The organic/aqueous distribution coefficients in Table 4 are reported as the concentration of the element in the organic phase divided by the concentration of the element in the aqueous phase.

Table 4. Batch Distribution Coefficients for U and Mo from Dissolved SK Material

Test	**U Distribution Coefficient***	**Mo Distribution Coefficient**
4M HNO$_3$		
Extract	2.511	< 0.0030§
Scrub	2.479	---
Strip	0.045	---
Wash	1.2x10^{-6}[†]	---
5M HNO$_3$		
Extract	2.649	< 0.0023§
Scrub	2.461	---
Strip	0.070	---
Wash	5.5x10^{-7}	---

--- element below detection limit in both phases; no valid distribution coefficient can be determined

*Data reported with ±20% uncertainty

§Data reported as less than values since the organic Mo was below detection limits

[†] Poor agreement between duplicate measurements

The batch distribution coefficients show U has a preference for the organic phase when the aqueous phase is 4-5 M HNO$_3$. There is little difference in the U distribution coefficients whether the aqueous phase is 4 M or 5 M HNO$_3$. Table 4 shows U distribution coefficients for the extraction step similar to those reported elsewhere with 7.5 vol % TBP in n-paraffin.(9) Thompson et al. report U distribution ratios of 2.76-3.56 for aqueous solutions that contain between 0.0132 M and 0.021 M U after extraction.(7)

In Table 2, batch distribution coefficients for Mo are less than 0.003. During extraction from either 4 M or 5 M HNO$_3$, mass balance calculations show greater than 99.9% of the Mo remains in the aqueous phase during solvent extraction and should exit the mixer-settlers in the 1st U cycle aqueous waste stream (1AW). Since greater than 99.9% of the Mo remains in the aqueous phase, the amount of Mo extracted into the organic was below the analytical detection limit and resulted in maximum distribution coefficients of 0.0030 from 4 M HNO$_3$ and 0.0023 from 5 M HNO$_3$. For the scrub, strip, and wash solvent extraction steps, the Mo content of both the organic and aqueous phases was below detection limit and prohibited the calculation of valid distribution coefficients.

In comparison to data from previous solvent extraction experiments using dissolved U-Mo fuel as feed, the Mo distribution coefficients from dissolved SK material are lower. In the literature, Mo distribution coefficients range from 0.0001 to 0.1 with 7.5% TBP/*n*-paraffin contacted with HNO$_3$.(5),(10),(11) Previous SRS projects involving miniature mixer-settler experiments for U recovery from dissolved Hallam(6) (90% U/10% Mo) and Piqua(7) (97% U/3% Mo) fuels show Mo distribution coefficients were 0.2-2 and 0.3-6, respectively, and the purity of the U products produced from those fuels was not affected. The aqueous feed for mixer-settler experiments with dissolved Hallam and Piqua fuels contained Fe and Al, respectively, which acted as salting agents to increase the distribution ratios. The dissolved SK material did not have added Al, and it had less Fe than Hallam feed, which resulted in lower Mo distribution coefficients.

Both the U and Mo batch distribution coefficients with SK feed material are lower than those obtained during solvent extraction with Piqua and Hallam feeds. The difference is likely due to the lack of Al^{3+} in the SK aqueous feed. In aqueous solutions, Al^{3+} has a high charge-to-size ratio, is highly hydrated, and acts as a salting agent which could increase metal ion distribution ratios.(12) Nelidow and Diamond report Mo distribution ratios with salts containing equivalent amounts of ammonium, calcium, or Al in the aqueous phase. The distribution ratios for Mo were the largest from solutions containing Al.(7)

U Product Specifications: The U product from this campaign will be sent to the SRS highly enriched U blend down program where ^{235}U will be blended with natural U prior to shipment to Tennessee Valley Authority (TVA) for use in reactor fuel preparation. The TVA specifications require < 200 µg Mo/g U, thus, the required purity of the H-Canyon U product prior to blending is 800 µg Mo/g U.

In H-Canyon operations, the 0.01 M HNO_3 strip solution is the product solution that is sent for blending with natural U to produce low enriched U for off-site shipment. Table 5 shows data used to calculate the Mo/U mass ratio in the 0.01 M HNO_3 strip solution. (Data are reported for the only test in which Mo was detected in the strip solution by ICPMS).

Table 5: Mo/U Ratio in U Strip Product

Initial Aqueous Phase	**Mo (mg/L)**	**^{235}U (g/L)**	**Product U (g/L)**	**µg Mo / g U**
4 M HNO_3	0.0584	1.6	7.8	7.48

Based on these results, it is reasonable to expect that after processing SK material in H-Canyon, the U product will contain less than 800 µg Mo/g U.

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