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SOLVENT EXTRACTION FOR URANIUM-MOLYBDENUM ALLOY DISSOLUTION FLOWSHEET

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SUMMARY

H-Canyon Engineering requested the Savannah River National Laboratory (SRNL) to perform two solvent extraction experiments using dissolved Super Kukla (SK) material. The SK material is an uranium (U)-molybdenum (Mo) alloy material of 90% U/10% Mo by weight with 20% ^{235}U enrichment. The first series of solvent extraction tests involved a series of batch distribution coefficient measurements with 7.5 vol % tributylphosphate (TBP)/n-paraffin for extraction from 4-5 M nitric acid (HNO_3), using 4 M HNO_3-0.02 M ferrous sulfamate ($Fe(SO_3NH_2)_2$) scrub, 0.01 M HNO_3 strip steps with particular emphasis on the distribution of U and Mo in each step. The second set of solvent extraction tests determined whether the 2.5 wt % sodium carbonate (Na_2CO_3) solvent wash change frequency would need to be modified for the processing of the SK material.

The batch distribution coefficient measurements were performed using dissolved SK material diluted to 20 g/L (U + Mo) in 4 M HNO_3 and 5 M HNO_3. In these experiments, U had a distribution coefficient greater than 2.5 while at least 99% of the nickel (Ni) and greater than 99.9% of the Mo remained in the aqueous phase. After extraction, scrub, and strip steps, the aqueous U product from the strip contains nominally 7.48 µg Mo/g U, significantly less than the maximum allowable limit of 800 µg Mo/g U.

Solvent washing experiments were performed to expose a 2.5 wt % Na_2CO_3 solvent wash solution to the equivalent of 37 solvent wash cycles. The low Mo batch distribution coefficient in this solvent extraction system yields only 0.001-0.005 g/L Mo extracted to the organic. During the solvent washing experiments, the Mo appears to wash from the organic.

INTRODUCTION

The SK Prompt Burst Reactor operated at the Nevada Test Site from 1964 to 1978. The SK produced an intense pulse of neutrons and gamma radiation and was used for neutron irradiation of test specimens, including weapons materials. The reactor configuration included rods, disks, and rings made of a U alloy. All the U components of the reactor were manufactured at Y-12 during the 1960s.

The SK U-Mo material at Y-12 consists of 4.7 metric tons of U. The total mass of the SK material with the Mo is 5.3 metric tons of material. The material is 90% U/10% Mo by weight at approximately 20% ^{235}U enrichment. Previous flowsheet development for the processing of U-Mo fuels at the Savannah River Site (SRS) during the 1970s and 1980s shows that any nickel (Ni) cladding associated with the material will dissolve readily and traditional solvent extraction flowsheets can be used to recover and purify the U.[1,2,3]

Before the solvent extraction experiments could be performed, the SK material was dissolved to establish optimum processing conditions.[4] Once the SK material was dissolved, the solutions contained primarily U and Mo with small amounts of Ni from the

0.005-inch plating on the surface of the SK material. Following dissolution in H-Canyon processing facilities, the dissolved material will be processed through solvent extraction and the U sent to the SRS highly enriched uranium (HEU) blend down program.

H-Canyon Engineering requested[5] that SRNL define a flowsheet for safe and efficient processing of the SK material. The flowsheet for U-Mo alloy dissolution is fairly well-characterized.[6] However, the following experimental work was recommended to define moderate-risk items for processing the SK materials.

1) Acid consumption studies with actual SK material to ensure that the dissolution conditions will preclude the precipitation of molybdenum oxide (MoO_3).
2) Mo solubility measurements for 20 g/L U and 1 g/L iron (Fe) at 100-105 ^oC in HNO_3.
3) Batch distribution coefficient measurements for extract, strip, and wash with particular emphasis on the distribution of Mo.
4) Computer modeling to confirm adequate U recovery and purification for 1st and 2nd U cycles.

Two other items were added later by H-Canyon Engineering.

5) Measurements of hydrogen gas (H_2) during dissolution of SK material in 1 M and 2 M HNO_3 with the understanding that higher HNO_3 conditions are less favorable for the formation of H_2.
6) Solvent wash studies to determine whether the presence of Mo in the aqueous feed will have an effect on solvent washing and the frequency of solvent wash replacement.

The solvent wash studies were necessary because H-Canyon operating criteria and the knowledge that Mo is removed from the 1st U cycle C-bank solvent (1CW) using a 2.5 wt % Na_2CO_3 wash.[7] In H-Canyon, there are four triggers for determining when to change the 2.5 wt % Na_2CO_3 solvent wash solution: 1) total wash time, 2) alkalinity, 3) U concentration, and 4) gamma activity. H-Canyon operating experience has shown that total wash time is almost always the trigger that determines when the solvent wash solution is changed. Procedurally, the trigger for total wash time is 800-1000 hours and each solvent wash cycle takes, nominally, 65 hours. As a result, a solvent wash solution is good for approximately 12 - 15 solvent wash cycles. H-Canyon requested additional experiments to determine whether the presence of Mo in the 1CW solvent would impact the 2.5 wt % Na_2CO_3 solvent wash change frequency.

This report addresses Items 3 and 6 of the recommended work. Items 1, 2, 4, and 5 will be addressed in other SRNL technical reports.

EXPERIMENTAL

Chemicals

TBP was used as received from Acros Chemicals and HNO_3 was used as received from Fisher Chemicals. $Fe(SO_3NH_2)_2$ and *n*-paraffin were obtained from quantities available within the Actinide and Chemical Technology Section.

U/Mo Aqueous Feed Preparation

Two aqueous solutions containing U and Mo were prepared as solvent extraction feed by diluting solutions produced from the SK dissolution experiments as detailed elsewhere.[4] First, an appropriate volume of a green 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 4-4.2 M HNO_3. Second, an appropriate volume of a yellow 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. The difference in the colors of the initial HNO_3 solutions is due to the presence of Ni in the 4 M HNO_3 solution and absence of Ni in the 5 M HNO_3 solution.

One aqueous solution was prepared for the solvent washing tests. Thirty milliliters of 33.3 g/L (U + Mo) in 5 M HNO_3 were combined with 29 mL of 35.5 g/L (U + Mo) in 4 M HNO_3.

Analyses

All ^{235}U content in organic and aqueous phases was quantified using gamma counting. Aqueous Mo was analyzed using Inductively Coupled Plasma Emission Spectroscopy (ICPES) and Inductively Coupled Plasma Mass Spectroscopy (ICPMS). Organic Mo was analyzed using Parr bomb combustion followed by ICPES and/or ICPMS. In addition, organic Mo was stripped from the organic with 2.5 wt % Na_2CO_3 and ICPES and/or ICPMS was used for analysis of the resulting aqueous solution. The isotopic distribution for Mo was assumed to be 15.9% ^{95}Mo and 84.1% ^{96}Mo. Nickel was analyzed using ICPES.

U-Mo Batch Distribution Coefficients

These experiments were performed in duplicate in a radiological glovebox. 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 (Scientific Industries model K-500-2 vortex test tube 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.

1. EXTRACT: Add 18 mL of 7.5 vol % TBP/n-paraffin and 18 mL of appropriate aqueous feed solution to a 40 mL glass tube. Vortex and allow phases to separate.

    1.1. Remove aliquots of organic and aqueous phases for gamma counting to quantitate ^{235}U.
    1.2. Remove an aliquot of the aqueous phase for ICPES and/or ICPMS.
    1.3. Remove 6 mL of organic phase and contact with 3 mL of 2.5 wt % Na_2CO_3. Analyze the aqueous phase by ICPES and/or ICPMS. Analyze the washed organic by Parr bomb dissolution followed by ICPES and/or ICPMS.

2. SCRUB: Add 10 mL of 7.5 vol % TBP/n-paraffin from the EXTRACT step and 10 mL of 4 M HNO_3/0.02 M ferrous sulfamate (FS) to a 40 mL glass tube. Vortex and allow the phases to separate.

    2.1. Remove aliquots of organic and aqueous phases for gamma counting to quantitate ^{235}U.
    2.2. Remove an aliquot of the aqueous phase for ICPES and/or ICPMS.
    2.3. Remove 6 mL of organic phase and contact with 3 mL of 2.5 wt % Na_2CO_3. Analyze the aqueous phase by ICPES and/or ICPMS. Analyze the washed organic for Parr bomb dissolution followed by ICPES and/or ICPMS.

3. STRIP: Add 5 mL of 7.5 vol % TBP/n-paraffin from the SCRUB step and 5 mL of 0.01 M HNO_3 to a 40 mL glass tube. Vortex and allow the phases to separate.

    3.1. Remove aliquots of organic and aqueous phases for gamma counting to quantitate ^{235}U.
    3.2. Remove an aliquot of the aqueous phase for ICPES and/or ICPMS.
    3.3. Remove 3 mL of organic phase and contact with 2 mL of 2.5 wt % Na_2CO_3. Analyze the aqueous phase by ICPES and/or ICPMS. Analyze the washed organic for Parr bomb dissolution followed by ICPES and/or ICPMS.

4. WASH: Data were obtained in step 3.3.

Solvent Wash Studies

Solvent wash studies were performed using volumes of solution detailed in Table 1. The organic/aqueous volume ratios were selected such that each cycle of the five cycles simulated seven contacts of the carbonate wash with the solvent.

1. EXTRACT: Add solvent and aqueous feed solutions to a glass tube, vortex, and allow phases to separate.

    1.1. Remove the aqueous phase from the glass tube.

2. STRIP: Add appropriate volume of 0.01M HNO_3 to the glass tube, vortex, and allow phases to separate.

   2.1. Remove the aqueous phase from the glass tube.
   2.2. Add fresh 0.01M HNO_3, vortex, and remove aqueous solution from the glass tube.
   2.3. Add fresh 0.01M HNO_3, vortex, and remove aqueous solution from the glass tube. Save an aliquot of the third strip solution for analysis.

Table 1: Solution Volumes Used for Solvent Washing Experiments

	Solution Volumes (mL)				
Solution	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Extract					
Solvent	28.35∬	22.68	17.01	11.34	5.67
Aq. Feed[†]	16.68	13.34	10.01	6.67	3.34
*Strip**					
Solvent	28.35	22.68	17.01	11.34	5.67
Strip (0.01 M HNO_3)	16.68	13.34	10.01	6.67	3.34
Wash					
Solvent	28.35	22.68	17.01	11.34	5.67
Wash (2.5 wt % Na_2CO_3)	3.75∬	3.00	2.25	1.50	0.75
Excess 1 M HNO_3	0.00363	0.00290	0.00218	0.00145	0.00073

*In each cycle, the strip consisted of contacting the solvent three times with the appropriate volume of fresh 0.01 M HNO_3.

∬The 7.5 vol % TBP/n-paraffin and 2.5 wt % Na_2CO_3 aliquots used in cycle 1 were re-used for cycles 2-5, but the volumes were appropriately adjusted.

[†] New aqueous feed was used in each cycle.

3. WASH: Add appropriate volumes of 2.5% Na_2CO_3 and excess HNO_3 to the glass tube, vortex, and allow phases to separate. (The excess HNO_3 was added due to entrainment of HNO_3 during solvent wash cycle. The amount of HNO_3 added corresponds to the amount of HNO_3 that would have been entrained in the solvent during normal solvent washing).

   3.1. Remove a 0.75 mL aliquot of the wash solution, add it to 2.25 mL of deionized water, and prepare samples for Mo analysis by ICPES or ICPMS and anion analysis by ion chromatography.
   3.2. Remove remaining solvent wash solution from the glass tube and save for use in remaining experiments.

RESULTS AND DISCUSSION

The compositions of the aqueous solutions used for solvent extraction feed are summarized in Table 2.

Table 2: Composition of Aqueous Solutions for Batch Solvent Extraction

Initial Solution	^{235}U (g/L)	Total U (g/L)	Mo (g/L)	Ni (g/L)	Fe (g/L)
4 M HNO_3	3.27	16.0	1.73	1.45	0.676
5 M HNO_3	3.40	15.8	1.83	< 0.001	0.676

Data reported with ±10% uncertainty

The SK material contains 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 2 confirms 20% ^{235}U enrichment in both solutions.

U-Mo Batch Distribution Coefficients

The organic/aqueous distribution coefficients in Table 3 are reported as the concentration of the element in the organic phase divided by the concentration of the element in the aqueous phase.

Table 3: Batch Distribution Coefficients for U, Mo, and Ni from Dissolved SK Material

Test	U Distribution Coefficient*	Mo Distribution Coefficient	Ni Distribution Coefficient*
4M			
Extract	2.511	< 0.0030§	< 0.0006
Scrub	2.479	---	---
Strip	0.045	---	---
Wash	1.2×10^{-6}†	---	---
5M			
Extract	2.649	< 0.0023§	---
Scrub	2.461	---	---
Strip	0.070	---	---
Wash	5.5×10^{-7}	---	---

Data reported as an average of two experiments.
--- 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

These batch distribution coefficients show that 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 3 shows U distribution coefficients for the extraction step similar to those reported elsewhere with 7.5 vol % TBP in n-paraffin.[8] 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.[8] The slightly lower U distribution coefficients for the SK material are likely due to the absence of aluminum (Al) from the aqueous feed solution.

Batch distribution coefficients for Mo in Table 3 reveal distribution coefficients 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 and should exit the first U cycle A-bank (1A) Bank in the 1st U cycle aqueous waste stream (1AW). In comparison to data from previous U-Mo solvent extraction experiments, the Mo distribution coefficients from dissolved SK material are lower. 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 the present experiments, the TBP was not washed with carbonate solution prior to use. If dibutylphosphate (DBP) were present in the TBP prior to use, DBP could impact the Mo distribution coefficient only if Mo was present in the solution as a positively charged species. With a positively charged Mo species, any DBP present could act to increase the Mo distribution coefficient rather than decrease it since, at low acid concentrations, the DBP would be an anion and could form a neutral extractable species with cationic Mo. However, any DBP present in the TBP would have little to no effect on Mo distribution coefficients since, in acidic solutions containing Mo at concentrations greater than 10^{-4} M, Mo polymerizes to form polymolybdates[9] which are negatively charged and neither extracted nor impacted by the presence by DBP. Both the 4 M and 5 M HNO_3 solvent extraction feed solutions contained nominally 0.02 M Mo.

ICPMS analysis of the 2.5 wt % Na_2CO_3 used to wash the organic phase (as detailed in the Experimental section) revealed the Mo content was less than 23 µg/L. However, these data were collected on samples that were over two months old and the potential formation of polymeric Mo species rendered the ICPMS data questionable. Furthermore, incorporation of that ICPMS data produced Mo distribution coefficients that were unlike any reported in the literature. The ICPMS data were determined to be unusable but the 2.5 wt % Na_2CO_3 wash of the solvent proved an efficient method to remove Mo from the solvent.

Previous tests confirm that the presence of both Fe and Ni in U solutions does not interfere with U recovery or contaminating the products.[7,10] SRS dissolution of Piqua fuel (96% U/4% Mo by weight clad in Al with 0.5 wt % Ni as a bonding agent) showed that Mo was extracted to the organic and the purity of U product was not affected.[7] The dissolved Piqua feed contained 0.11-0.48 M Al which, in aqueous solutions, has a high charge-to-size ratio, is highly hydrated, and acts as a salting agent to increase the distribution ratios.[11] 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.[11]

Ni was present at measurable quantities only in the 4 M HNO_3 aqueous feed solution and, as shown in Table 3, has a distribution coefficient significantly less than 1.0 during the extraction. In the literature, Ni is not appreciably soluble in TBP/n-paraffin and is separated effectively from the U product in the first cycle and retained in the waste stream.[12] During these batch solvent extraction experiments, such a small amount of Ni was extracted to the organic phase that, in subsequent scrub, strip, and wash steps, the Ni was below the detection limit in both phases. In these experiments, within the limits of analytical uncertainty, greater than 99% of the Ni remains in the aqueous phase. Thus, any Ni present in the 1AF solution should remain in the aqueous phase and exit the 1A Bank in 1AW.

U Product Specifications

In H-Canyon operations, the 0.01 M HNO_3 strip solution is sent for blending with natural U to produce low enriched U for off-site shipment. The Tennessee Valley Authority (TVA) requirements for their product is 200 µg Mo/g U, which requires the H-Canyon product to contain less than 800 µg Mo/g U. Table 4 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 4: Mo/U Ratio in U Strip Product

Initial Aqueous Phase	Mo (mg/L)	^{235}U (g/L)	Total 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 product will contain less than 800 µg Mo/g U.

Solvent Wash Studies

A series of experiments was performed to assess whether Mo present from dissolved SK material impacts the lifecycle of the 2.5 wt % Na_2CO_3 wash solution. Figure 1 summarizes the data for Mo content of the 2.5 wt % Na_2CO_3 and the third contact of the strip solution for each cycle.

In Figure 1, the volume ratio of solvent:carbonate wash used in each cycle was 7.56:1 and, after five cycles, the carbonate wash solution had been exposed to the equivalent of 37 contacts with 7.5 vol % TBP/n-paraffin. (The Na_2CO_3 and 7.5 vol % TBP/n-paraffin solutions were re-used from Cycle #1 in Cycles 2-5.) The aqueous feed for these experiments contained nominally 3.2 g/L Mo. Accounting for the volume of solution in each phase, the amount of Mo present in the wash in cycles 1-5 is 0.02-0.05% of the initial Mo added in each cycle. The low content of Mo in the wash solution is not surprising since the majority of the Mo is rejected by the solvent during extraction. Since the Na_2CO_3 solution was re-used and sampled after Cycles 2-5, a trend of increasing Mo content in the wash solution was expected but, as shown in Figure 1, did not occur (within the ±20% uncertainty of the data). Analysis of the organic phase for determination of the batch distribution ratios confirms a very low Mo content after the carbonate wash step (by ICPMS) and shows that Mo does not collect in the solvent phase.

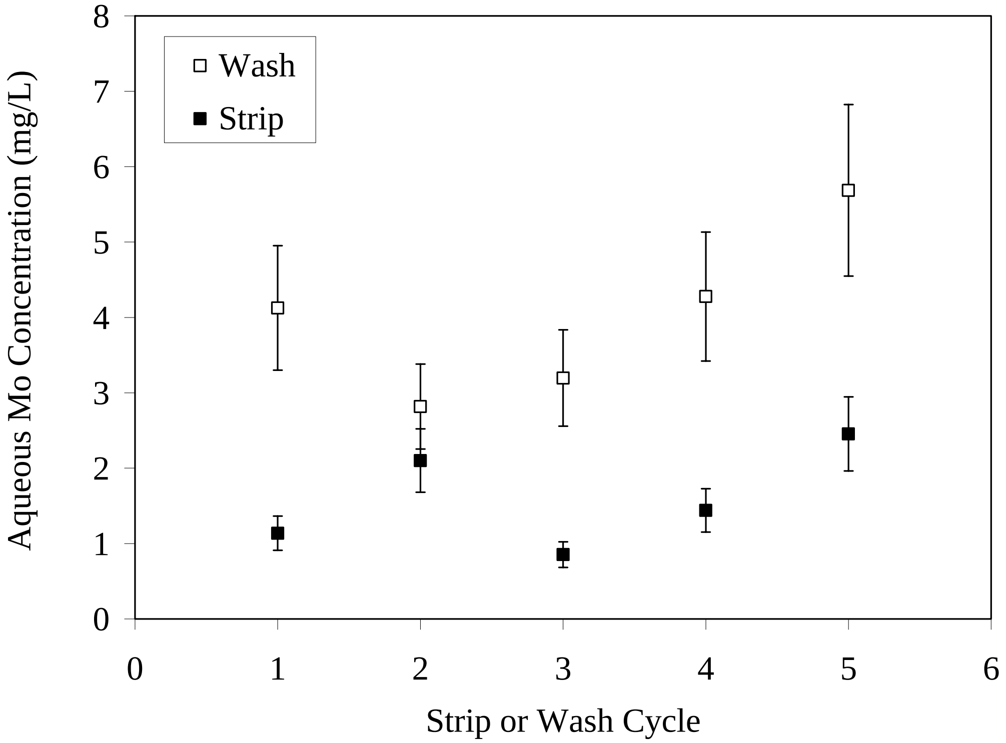

Figure 1: Aqueous Mo Content of Aqueous Strip and Wash Solutions

CONCLUSIONS

SRNL solvent extraction experiments with dissolved SK material confirmed the distribution ratios for U and Mo are acceptable during extraction. Valid distribution coefficients were not obtained for scrub, strip, or washing steps due to low Mo content. The U product from solvent extraction processes will contain nominally 7.48 µg Mo/g U. Furthermore, after the equivalent of 37 solvent washing cycles, the presence of Mo in the dissolved SK material does not adversely impact the quality of the solvent wash and, therefore, does not require departure from the current 12-15 solvent cycles for each solvent wash.

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