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URANIUM-MOLYBDENUM DISSOLUTION FLOWSHEET STUDIES

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SUMMARY

The Super Kukla (SK) Prompt Burst Reactor operated at the Nevada Test Site from 1964 to 1978. The SK material is a uranium-molybdenum (U-Mo) alloy material of 90% U/10% Mo by weight at approximately 20% ^{235}U enrichment. H-Canyon Engineering (HCE) requested that the Savannah River National Lab (SRNL) define a flowsheet for safely and efficiently dissolving the SK material. The objective is to dissolve the material in nitric acid (HNO_3) in the H-Canyon dissolvers to a U concentration of 15-20 g/L (3-4 g/L ^{235}U) without the formation of precipitates or the generation of a flammable gas mixture.

Testing with SK material validated the applicability of dissolution and solubility data reported in the literature for various U and U-Mo metals. Based on the data, the SK material can be dissolved in boiling 3.0-6.0 M HNO_3 to a U concentration of 15-20 g/L and a corresponding Mo concentration of 1.7-2.2 g/L. The optimum flowsheet will use 4.0-5.0 M HNO_3 for the starting acid. Any nickel (Ni) cladding associated with the material will dissolve readily. After dissolution is complete, traditional solvent extraction flowsheets can be used to recover and purify the U.

Dissolution rates for the SK material are consistent with those reported in the literature and are adequate for H-Canyon processing. When the SK material dissolved at 70-100 ^{o}C in 1-6 M HNO_3, the reaction bubbled vigorously and released nitrogen oxide (NO) and nitrogen dioxide (NO_2) gas. Gas generation tests in 1 M and 2 M HNO_3 at 100 ^{o}C generated less than 0.1 volume percent hydrogen (H_2) gas. It is known that higher HNO_3 concentrations are less favorable for H_2 production. All tests at 70-100 ^{o}C produced sufficient gas to mix the solutions without external agitation. At room temperature in 5 M HNO_3, the U-Mo dissolved slowly and the U-laden solution sank to the bottom of the dissolution vessel because of its greater density. The effect of the density difference insures that the SK material cannot dissolve and concentrate within the charge bundles.

Solubility behavior of the SK material during dissolution at 70 ^{o}C reflected data reported in the literature for 100 ^{o}C. When solutions containing solids at 70 ^{o}C were heated to 105 ^{o}C, the solids dissolved. After 21 days, the samples that had been heated closely resembled the non-heated ones with respect to solids content. Super-saturated solutions of U-Mo have been produced which can be stable for more than 10 days, but these conditions are outside of the bounds of the recommended flowsheet. It is not known how the different dissolution pathways affect solution stability, but the results agree with the fact that solubility should not be affected by the dissolution pathway. Therefore, the literature data should be used as the bounding condition for solubility.

Dissolution of the SK material consumed 2.8-8.0 moles of acid per mole of metal dissolved, which agrees with behavior reported elsewhere for U and U-Mo metals. The acid consumption values confirmed that a starting acid concentration in the dissolver of 4.0-5.0 M HNO_3 will allow H-Canyon Operations to avoid adjusting the feed from the dissolver prior to solvent extraction while providing maximum operating margin for avoiding precipitate formation.

INTRODUCTION

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

The SK uranium-molybdenum (U-Mo) material consists of 4.7 metric tons of U. The total mass of the material with the molybdenum is 5.3 metric tons of material. The material is 90% U/10% Mo by weight at approximately 20% ^{235}U enrichment. The SK reactor consisted of 19 annular rings, 5 disks and multiple rods. The rods will not be dissolved in H-Canyon. The rings and disks originally contained a 0.005-inch nickel plating. The rings and disks will be cut or cast and loaded into carbons steel cans for transport to SRS.

The objective is to dissolve the material in nitric acid (HNO_3) in the H-Canyon dissolvers to a U concentration of 15-20 g/L (3-4 g/L ^{235}U) without the formation of precipitates. Dissolution of the SK will be performed in 4-6 M HNO_3 using reusable stainless steel charging bundles. The material will be charged in carbon steel cans and the charging bundles will have carbon steel end caps; the carbon steel will contribute approximately 1.0-2.3 g/L iron to the solution. Small amounts of nickel (Ni) will also dissolve into solution from the 0.005-inch plating on the surface of the material. Aluminum is not part of the feed stream, which eliminates the need to add either mercury or potassium fluoride. Following dissolution, the dissolved material will be processed through 1st and 2nd Cycle solvent extraction and the U sent to the HEU blend down program. The flowsheet must also consider any aqueous waste processing and solvent recycle issues.

HCE requested that the SRNL define a flowsheet for safely and efficiently processing the SK material. The flowsheet definition is occurring in two phases. The first phase involved the evaluation of all available data related to the dissolution and solvent extraction of U-Mo materials to identify if a viable flowsheet for H-Canyon can be developed.

During the first phase it was determined that the flowsheet is fairly well-characterized *(1)*. The following experimental work was recommended to better define moderate-risk items:

1) Acid consumption studies with actual SK material to ensure that the dissolution conditions will preclude the precipitation of MoO_3.
2) HNO_3-Mo solubility measurements for 20 g/L U and 1 g/L Fe at 100-105 °C.
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 higher LEU [U] feed concentration versus that for HEU feed for 1st & 2nd U cycles.

Two other items were added later by HCE.

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 the effect on solvent washing and the frequency of solvent wash change out.

The second phase of the flowsheet definition provides a final recommended flowsheet based on new SRNL analyses and the literature data. This report addresses Items 1, 2, and 5 of the recommended work. Items 3, 4, and 6 will be discussed in other SRNL technical reports.

EXPERIMENTAL

Material Dissolution and Solubility

Dissolution rate and solubility tests were initiated in 500 mL of HNO_3. 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 [$Fe(NO_3)_3$-$9H_2O$]. The dissolution vessel is shown in Figure 1. The vessel cover contained penetrations for a thermocouple, check valve, and sample basket holder. Figure 1 currently shows a corrosion coupon in the basket in place of the SK sample. The vessel was placed on a hot plate with temperature and stirring control capabilities.

To sequentially dissolve the sample, the acid in the vessel was heated to temperature. Some dissolutions were performed at ~100 ^oC and others at ~70 ^oC. According to the literature, Mo solubility decreases with increasing temperature *(2)*. The SK sample (container ID# 5093414), received from Oak Ridge, was placed in the sample basket with the sample holder raised to its highest point to prevent the sample from touching the acid when the cover was placed on the bottom half of the vessel.


Figure 1. Dissolution Test Vessel

Successive dissolutions were performed by lowering the sample into the acid for a specific amount of time, pulling the sample out of the dissolver, rinsing the sample with deionized water, drying the sample and weighing it. This step introduced the potential for forming an oxide coating on the sample surface. Linear dimensions were periodically measured to approximate the surface area of the sample. The volume of the acid solution was occasionally measured to account for volume losses from acid consumption and evaporation. During the dissolution tests, aliquots of the acid solution containing increasing concentrations of SK were set aside for analysis and subsequent testing. Liquid samples of the acid solution were submitted for analysis by inductively-coupled plasma mass spectrometry (ICPMS), inductively-coupled plasma emissions spectrometry (ICPES), total acid/free acid, and gamma spectroscopy. At the end of the dissolution tests, eight samples were collected (Table 1) for subsequent testing.

Table 1. Test Solutions Prepared from Dissolution Studies

Start HNO_3 (M)	T (^oC)	SK (g/L)	Volume (mL)	Start HNO_3 (M)	T (^oC)	SK (g/L)	Volume (mL)
4	100	35.5	100	5	70	32*	255
4	70	44*	315	6	100	14	100
5	100	22	100	6	70	20*	100
5	70	28*	100	6	70	23*	258
* Precipitate present							

Aliquots (50-75 mL) of each of the samples in Table 1 were separated and placed in another test vessel (Figure 2). The vessel was equipped with a thermocouple and a check valve. The vessel was also designed with a cold finger down the center of the vessel to facilitate condensation of vapors. The cold finger was filled with room-temperature water at the start of the test. The solution in the vessel was heated to 105 ^oC and allowed to reflux for 60 min at 105 ^oC. For samples that contained a precipitate, the contents were shaken to provide for the presence of solids in the test. After heating, the solutions were cooled to room temperature and sampled for analysis by ICPMS, ICPES, total acid/free acid, and gamma spectroscopy.

Figure 2. Reflux Test Vessel

Gas Generation

Gas generation occurred in a manner similar to material dissolution tests using the vessel shown in Figure 1. The only change to the test apparatus is that the check valve was replaced with a 1-liter Tedlar® gas sample bag. Two gas generation tests were conducted in 1000 mL of HNO_3, one each at 1 M and 2 M HNO_3. The nominal head space above the liquid was 250 mL. The vessel was placed on a hot plate with temperature and stirring control capabilities. The SK sample was placed in the sample basket with the sample holder raised to its highest point to prevent the sample from touching the acid when the cover was placed on the bottom half of the vessel. The solution was heated to 100 ^oC prior to initiating a test.

Once at temperature, three successive dissolutions were performed without opening the vessel to obtain three gas samples. Successive dissolutions were performed by lowering the sample into the acid for a specific amount of time, and then raising it back out of solution to change the gas sample bag. Because there was still gas generation occurring from solution during the bag change, additional air was not introduced into the system. Dissolution was conducted until each gas sample bag contained 500-800 mL of gas. After the dissolutions were complete, the gas sample bags were exhausted through 22-mL glass sample bulbs purged with argon. The gas sample bulbs were submitted for analysis using gas chromatography (GC).

RESULTS AND DISCUSSION

Material Dissolution

When the SK material dissolved at 70-100 ^{o}C in 1-6 M HNO_3, the reaction bubbled vigorously and released nitrogen oxide (NO) and nitrogen dioxide (NO_2) gas. Nitrogen dioxide, an orange-brown gas, was present in the vessel head space. The presence of NO, which is colorless, was observed based on a more intense orange-brown color when the head space gas was allowed to react with air; NO reacts with oxygen (O_2) to form NO_2. A significant portion of the bubbling that occurred during dissolution resembled the action of a boiling liquid, which produces a larger bubble size than the metal dissolution reaction.

During dissolution at 100 ^{o}C, sufficient gas generation occurred from combined metal dissolution and boiling to agitate the entire solution without the aid of stirring. At 70 ^{o}C, gas generation from the dissolution of the sample was sufficient to agitate the solution without external agitation. The findings were comparable to those observed for the dissolution of U metal which demonstrated that U cannot concentrate in the charge bundles as it dissolves at elevated temperatures *(3)*. Accumulation of dissolved U in the charge bundles is one theoretical criticality scenario. Observations were made of the dissolution characteristics of the SK material in 5 M HNO_3 at room temperature. The behavior mirrored that of the U metal at 4 M HNO_3 in that the U dissolved slowly and the U-laden solution sank to the bottom of the dissolution vessel because of its greater density. This result confirms that when the material is charged to the dissolver at room temperature, it does not dissolve and concentrate inside of the charge bundles.

Dissolution rates for U, Mo and U-Mo have been previously reported for 4 M HNO_3 at 100-105 ^{o}C. Uranium metal dissolves at 105 ^{o}C in 4 M HNO_3 at 0.309 mg/min-cm^2 and in 7 M HNO_3 at 1.285 mg/min-cm^2. In 2 M HNO_3 at 100 ^{o}C, the dissolution rate for U metal is 0.051 mg/min-cm^2 *(3)*. Molybdenum metal dissolves faster than U. In 4 M HNO_3 at 90 ^{o}C, the dissolution rate of Mo is 16 mg/min-cm^2 *(4)*. The literature also report dissolution rates for U-Mo materials in HNO_3. For U-3Mo alloy, dissolution rates in boiling HNO_3 are 30 mg/min-cm^2 in 4 M HNO_3 and 43 mg/min-cm^2 in 5 M HNO_3. *(5)*

Experiments with SK yielded similar results, as shown in the data of Table 2. The dissolution rates are somewhat lower than those reported in the literature for the U-3Mo material. The difference may be attributable to the formation of an oxide coating on the sample when the sample was weighed. For both 74 and 100 ^{o}C, the data show the expected increase in dissolution rate as a function of acid concentration and temperature. The data for 4 M HNO_3 show more scatter than the other acid concentrations. The variance was probably caused by evaporative losses. The losses were less for the 5 M and 6 M HNO_3 experiments because the dissolution times and masses of material dissolved were reduced. The solution volume data are included in (Table 4).

Table 2. SK Material Dissolution Rates in HNO_3 with 1 g/L Fe.

Starting HNO_3 (M)	Temp (°C)	Time (min)	Dissolved Mass (g)	Dissolution Rate (mg/min-cm^2)
1 (no Fe)	100	90	5.085	1.6
4	100	5	1.834	8.5
4	100	10	4.868	11.4
4	100	12	6.963	13.8
4	74	9	2.954	8.1
5	99	4	2.730	17.8
5	99	6	4.064	17.8
5	100	5	3.664	19.6
5	74	3	1.190	10.8
6	100	2	1.793	22.3
6	100	3	2.856	23.9
6	100	2	2.011	25.6
6	70	5	2.141	11.0
6	73	2	0.852	11.0

Table 3. Acid Consumption during SK Metal Dissolution

Start HNO_3 (M)	Calc. U-Mo (g/L)	Temp (deg. C)	Solution Volume (mL)	Pro-rated Volume (mL)	Total Acid (M)	Free Acid (M)	Pro-rated Free Acid (mol)	mol acid: mol metal
4	0	100	500	1000	4.0	4.00	4.00	---
4	35.6	95	425	850	4.22	3.46	2.94	6.63
4	35.6	74	325	850	4.22	3.46	2.94	---
4	45.0	74	315	824	4.19	3.42	2.82	2.93
5	0	100	500	1000	5.0	5.00	5.00	---
5	22.3	100	470	940	5.18	4.39	4.13	8.73
5	22.3	64	370	940	5.18	4.39	4.13	---
5	27.8	64	360	915	5.23	4.39	4.02	4.52
5	27.8	74	260	914	5.23	4.39	4.01	---
5	32.4	74	258	907	5.17	4.36	3.95	2.81
6	0	100	500	1000	6.0	6.00	6.00	---
6	14.0	100	475	950	6.4	5.40	5.13	13.85
6	14.0	66	375	950	6.4	5.40	5.13	---
6	20.0	70	360	912	6.4	5.39	4.92	7.96
6	20.0	70	260	912	6.42	5.39	4.92	---
6	23.3	73	255	894	6.41	5.41	4.84	5.18

Samples from the dissolution experiments were submitted for analysis by total and free acid. The data are shown in Table 3. Also included in Table 3 are experimental volumes. A separate column titled "pro-rated volume" was calculated to normalize the data to 1000 mL and allow comparison of acid consumption as a function of metal dissolution. The acid consumption calculation assumes an average molecular weight of 222.9 g/mol for the SK material.

The acid consumption values ranged from 2.8-13.9 moles of acid per mole of metal. The highest acid consumption values occur during the early stages of each experiment where the dissolution temperature is ~100 ^oC and evaporative losses may influence the data, particularly since no condenser was used during the experiments. The latter parts of each experiment, which were conducted at ~74 ^oC, show acid consumption values ranging from 2.8-8.0. The acid consumption values agree with reported values.

SRS operating experience is that 4.0-4.5 moles of HNO_3 are consumed per mole of U metal dissolved *(6)*. Since U comprises almost 90% of the overall SK material, assuming 4.0-4.5 moles of HNO_3 consumption per mole of material is a good estimate. That estimate is further supported by experience from dissolving U-Mo fuels. For the Piqua fuels (U-3Mo), which contained Al cladding, similar acid consumption values were measured in the plant. The process flowsheet dissolved enough material to yield a metal concentration of 0.72 M metal with the consumption of 3.0 M of HNO_3 for a consumption of 4.2 moles of HNO_3 per mole of metal *(7)*. Studies at Oak Ridge with U-Mo alloys measured typical acid consumption of 3.5-5.5 moles of HNO_3 per mole of material regardless of whether the alloy contained 3%, 8.4%, or 10% Mo *(8)*.

The acid consumption data of Table 3 have been plotted along with U-Mo solubility reported by Faugeras *(2)* in Figure 3. Also included in Figure 3 is a calculated acid consumption line for a simulated dissolution of SK material in H-Canyon *(1)*. Figure 3 shows that the experimental acid consumption values do not differ greatly from the calculated acid consumption profile for SK dissolution. The main reason that the variance is not significant is because the amount of metal dissolved is relatively small compared to the amount of acid in the dissolver.

The acid loss data from the SK tests and the literature both indicate that a final dissolver solution nitrate concentration of 4-5 M with 15-20 g/L total U and 1.7-2.2 g/L Mo can be attained without forming a precipitate. The formation of precipitates will be discussed in the next section. A starting acid concentration in the dissolver of 4.5-5.0 M HNO_3 will allow H-Canyon Operations to avoid adjusting the feed from the dissolver prior to solvent extraction while providing maximum operating margin for avoiding precipitate formation.

It is worth noting that the SK material contains Ni plating, which dissolves readily. Nickel will comprise less than 0.5% of the total mass of the actual SK material. As will be shown Table 6, Ni 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 readily dissolved into HNO_3 and did not yield a precipitate *(9)*.

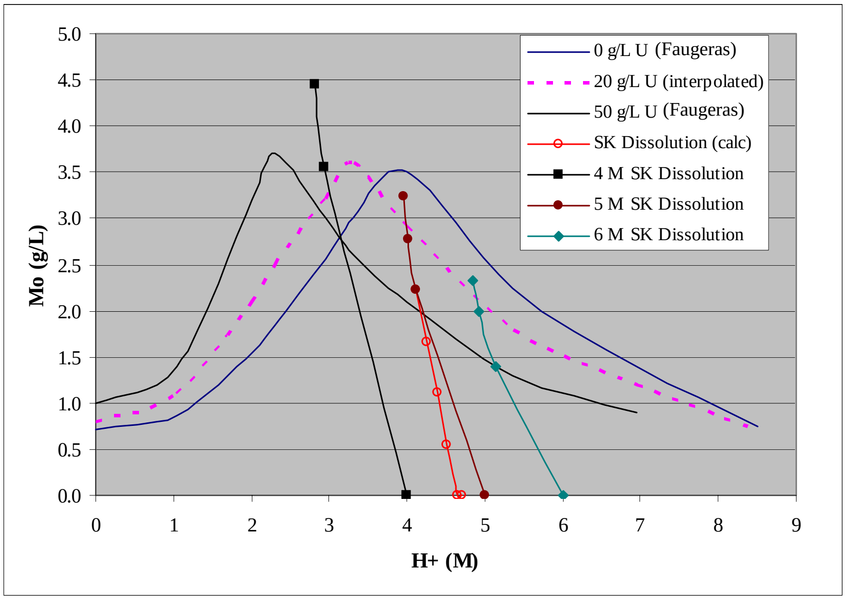

Figure 3. SK Dissolution Profiles *(1, 2)*

Solubility

Dissolution studies were performed in 4 M, 5 M and 6 M HNO_3 with 1 g/L ferric nitrate to confirm operating conditions that would preclude the formation of precipitates. Based on data in the literature that indicates Mo solubility decreases with increasing temperature, the first stages of the dissolution were performed at ~100 ^oC followed by dissolution at ~70 ^oC. Molybdenum solubility data in 2 M HNO_3 have been reported as a function of temperature: 2 g/L at 100 ^oC, 3 g/L at 70 ^oC, 6 g/L at 50 ^oC, and 20 g/L at 25 ^oC; more limited data for 4 M HNO_3 show a similar trend *(2)*. The objective of the dissolution tests was to maintain the dissolution at 100 ^oC at conditions that would not be saturated, and then obtain higher concentrations of soluble SK at 70 ^oC. The more-concentrated U-Mo solutions could then be heated to 100-105 ^oC and, because of decreasing Mo solubility with increasing temperature, would precipitate and permit solubility measurements at 100-105 ^oC.

It was observed that the dissolutions at 100 ^oC were successful in maintaining the solution conditions below the solubility limit for the SK material. However, when additional dissolutions were performed at ~70 ^oC, precipitates were observed (Figure 4). Experimental measurements for the tests are tabulated in Table 4. The precipitation observed at ~70 ^oC was contrary to expectations based on the literature. The formation of the solids, however, is a byproduct of the experimental method. Each time the sample is removed from solution to obtain a weight, the hot sample is able to react with air and form an oxide coating. When the solution is re-introduced into the solution, the oxide coating detaches from the metal surface and does not dissolve readily in HNO_3. The work of Faugeras et al. achieved solubility data by dissolving molybdic oxide (MoO_3) into solutions of uranium, which differs from the path to solubility for the current tests. It is known that the manner of reaching solubility can affect the time required to reach equilibrium (i.e. the formation super-saturated solutions). Solubility, on the other hand, is not affected by the means used to arrive at equilibrium.

Table 4. Formulation of SK Solubility Samples

4 M HNO_3 Dissolution of SK Material

Total Time (min)	Temp (deg. C)	Mass Dissolved (grams)	Volume (mL)	Calculated U-Mo conc. (g/L)
0	100	---	500	---
5	100	1.834	487*	---
15	100	4.868	462*	---
27	100	6.963	432*	---
30	95	1.454	425	35.6
---	72	100 mL Sample	325	---
39**	74	2.954	315	45.0

5 M HNO_3 Dissolution of SK Material

Total Time (min)	Temp (deg. C)	Mass Dissolved (grams)	Volume (mL)	Calculated U-Mo conc. (g/L)
0	99	---	500	---
4	99	2.730	491*	---
10	99	4.064	481*	---
15	100	3.664	470	22.3
---	64	100 mL Sample	370	---
23**	64	2.000	360	27.8
---	72	100 mL Sample	260	---
26**	74	1.190	258	32.4

6 M HNO_3 Dissolution of SK Material

Total Time (min)	Temp (deg. C)	Mass Dissolved (grams)	Volume (mL)	Calculated U-Mo conc. (g/L)
0	100	---	500	---
2	100	1.793	493*	---
5	100	2.856	483*	---
7	100	2.011	475	14.0
---	66	100 mL Sample	375	---
12**	70	2.141	360	20.0
---	70	100 mL Sample	260	---
14**	73	0.852	255	23.3

* Interpolated volume value based on dissolved mass
** Fine brown precipitate observed in final solution

It was observed that the SK sample, which began as a clean metal, developed an oxide coating when removed from the dissolver solution. The color of the oxide coating resembled the color of the solids observed during testing (Figure 4). 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 cannot 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. *(5)*

Although the literature indicates that U-Mo solids can form, the conditions for producing those solids were markedly different from the SRNL experiments. *(5, 8)* First, the dissolver will be operated at conditions which preclude Mo precipitation. Second, if the dissolver acid concentration deviates from the flowsheet target of 4.0-5.0 M HNO_3, the amount of Mo that might precipitate is a small fraction of the total Mo. For 20 g/L U, Mo is soluble at 2.2 g/L Mo at acid concentrations ranging from 2.2-5.0 M HNO_3 (Figure 3). Therefore, an acid concentration as low as 3.0 M HNO_3 will not yield a precipitate while an acid concentration as high as 6.0 M HNO_3 *might* cause Mo solubility to decrease from 2.2 to 1.5 g/L. SRNL tests indicate that material dissolved in 6 M HNO_3 at 100 °C to concentrations as high as 2.3 g/L Mo with ~21 g/L U does not readily precipitate. If U-Mo solids happen to form, they are flocculent and can be removed with a centrifuge and then washed (5*)*. Studies have indicated that most of the U in the solids can be removed by washing with acid.

4 M HNO_3/44 g/L U-Mo **5 M HNO_3/32 g/L U-Mo** **6 M HNO_3/23 g/L U-Mo**

Figure 4. Solids Precipitated from Dissolution Studies

Following the initial dissolution experiments, the five samples containing solids were refluxed at ~105 °C for 60 min to facilitate further precipitation and measurement of U-Mo solubility at 105 °C. Although, based on the literature, it was expected that the amount of precipitate in the samples would increase with increased temperature, the opposite occurred. For all five samples, the solids dissolved. Analyses of the samples were performed. The ICPES, ICPMS and gamma data for the refluxed and non-refluxed samples are contained in Tables 5 and 6.

The information of Figure 3 is shown again in an altered form in Figure 5 to highlight precipitation behavior after one day in comparison to what was reported in the literature. Recognizing that Mo solubility is a function of U concentration and that the magenta line of Figure 5 will move to the left or right, depending on the actual U concentration, six of the eight data points plotted in Figure 5 are in clear agreement with the literature data. If the interpolated curve for 20 g/L U is reliable, the data point for 6 M HNO_3 (initial) with 18 g/L U should be soluble, although not by much. It is questionable whether the 4 M HNO_3 (initial) sample with 32 g/L U would be soluble based on interpolation of literature data.

The samples were viewed periodically after the initial tests. After 21 days, the solutions equilibrated to where the reflux samples resembled the non-reflux samples. In particular, the 4 M HNO_3 (initial) sample with 40 g/L U had solids in the refluxed solution of a quantity similar to the non-reflux sample. The 5 M HNO_3 (initial)/28 g/L U-Mo and 6 M HNO_3 (initial)/20 g/L U-Mo samples no longer had solids – solids from the non-reflux solutions dissolved. The non-reflux 5 M HNO_3 (initial)/23 g/L U-Mo sample also had no solids, but most of the solids had been previously removed for analysis. The 6 M HNO_3 (initial)/23 g/L U-Mo reflux sample did not have a precipitate after 21 days; however, the corresponding non-reflux sample still had a trace amount of solids, although only about 10% of what was originally present (Figure 4). When the above data are plotted against the literature data (Figure 6), excellent agreement occurs.

It should be noted that the dissolution data for 4 M HNO_3 are skewed because of the dissolution of a Ni coating on the surface of the metal. The samples from the solutions of the 4 M HNO_3 test show approximately 2.3 g/L Ni (Table 6). Consequently, when the Ni effect is removed, the actual total U and Mo drop to about 30 g/L and 3.4 g/L, respectively. The removal of the Ni effect moves the data point into a region where complete solubility is likely. Overall, the data support the reliability of interpolation of Mo solubility at 20 g/L U (Figure 5) as a worst-case scenario.

Some additional comments are appropriate about the ICPMS, ICPES and gamma data of Tables 5 and 6. First, the nominal uncertainties of the three methods are 20%, 10% and 1%, respectively. Therefore, the U data can be used for ^{235}U accountability, but cannot be used to establish an accurate isotopic value for the SK material. Furthermore, with the high degree of uncertainty associated with ICPMS and ICPES, significant variability between the data of Tables 5 and 6 should be expected, and perhaps even within a single table. The inner-table variability can be seen in the ICPMS U:Mo data of Table 5. The first seven samples yielded values of 3.11-3.36, and then a step change occurs for the next seven values to 3.56-3.82. The step change can be attributed to the application of different standard measurements to each set of seven samples. The variability underscores the sensitivity of ICPMS data.

Table 5. ICPMS Sample Data

Start HNO_3 (M)	Calc. U-Mo (g/L)	Reflux	ICPMS ^{235}U (g/L)	ICPMS ^{238}U (g/L)	ICPMS ^{234}U (g/L)	ICPMS %^{235}U	ICPMS ^{95}Mo** (g/L)	ICPMS Total Mo (g/L)	ICPMS U:Mo
4	35.6	No	5.17	22.80	0.049	18.5	0.56	3.55	3.19
4	35.6	Yes	5.38	23.22	0.051	18.8	0.57	3.60	3.21
4	45.0	No*	6.97	29.68	0.056	19.0	0.73	4.57	3.24
4	45.0	Yes	7.31	31.31	0.072	18.9	0.74	4.66	3.36
5	22.3	No	3.24	14.28	0.034	18.4	0.36	2.28	3.11
5	27.8	No*	4.41	19.58	0.033	18.4	0.49	3.07	3.16
5	27.8	Yes	4.79	20.45	0.043	18.9	0.51	3.20	3.19
5	32.4	No*	5.81	24.30	0.047	19.3	0.54	3.42	3.56
5	32.4	Yes	5.52	23.71	0.052	18.9	0.51	3.22	3.67
6	14.0	No	2.54	10.66	0.022	19.2	0.24	1.48	3.61
6	20.0	No*	3.39	14.74	0.028	18.7	0.33	2.05	3.58
6	20.0	Yes	4.46	19.52	0.034	18.6	0.42	2.64	3.67
6	23.3	No*	4.14	17.89	0.035	18.8	0.37	2.33	3.82
6	23.3	Yes	4.50	19.54	0.044	18.7	0.42	2.67	3.65

* Precipitate present

** Mo-95 is 15.9% of naturally occurring Mo. Mo-96 cannot be measured without interferences

Table 6. ICPES and Gamma Spectroscopy Sample Data

Start HNO_3 (M)	Calc. U-Mo (g/L)	Reflux	Gamma ^{235}U (dpm/mL)	Gamma ^{235}U (g/L)	ICPES U (g/L)	ICPES Mo (g/L)	ICPES Ni (g/L)	ICPES Fe (g/L)	ICPES U:Mo
4	35.6	No	2.74E+04	5.71	28.3	3.03	2.35	1.09	3.77
4	35.6	Yes	2.80E+04	5.84	28.0	3.05	2.34	1.10	3.71
4	45.0	No*	3.67E+04	7.65	37.1	3.75	2.29	1.07	4.00
4	45.0	Yes	3.57E+04	7.44	35.5	3.79	2.32	1.09	3.78
5	22.3	No	1.66E+04	3.46	18.3	2.11	0	1.03	3.50
5	27.8	No*	2.20E+04	4.59	23.1	2.42	0	1.00	3.86
5	27.8	Yes	2.45E+04	5.11	25.7	2.66	0	1.10	3.90
5	32.4	No*	2.58E+04	5.38	27.0	2.79	0	0.99	3.91
5	32.4	Yes	2.62E+04	5.46	25.8	2.77	0	0.99	3.76
6	14.0	No	1.11E+04	2.31	11.8	1.34	0	1.07	3.56
6	20.0	No*	1.61E+04	3.36	16.7	1.85	0	1.05	3.65
6	20.0	Yes	2.08E+04	4.34	21.8	2.23	0	1.34	3.95
6	23.3	No*	1.87E+04	3.90	19.7	2.15	0	1.07	3.70
6	23.3	Yes	2.09E+04	4.36	22.0	2.32	0	1.15	3.83

* Precipitate present

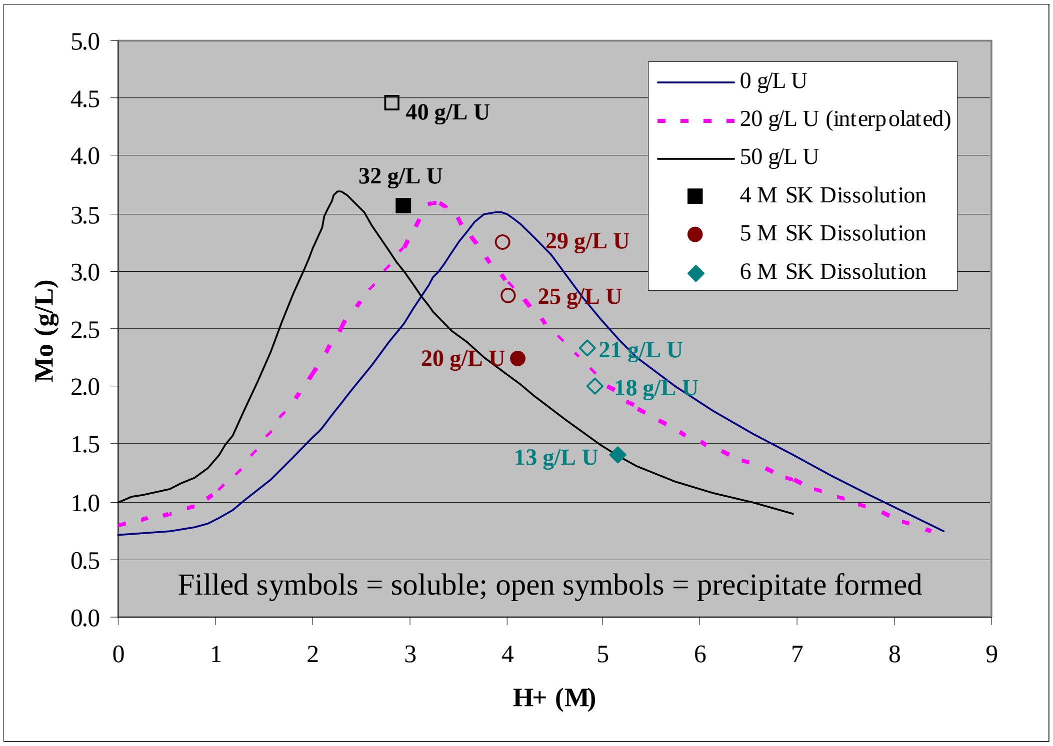

Figure 5. SK Solubility Data vs. Literature Values – One Day after Tests

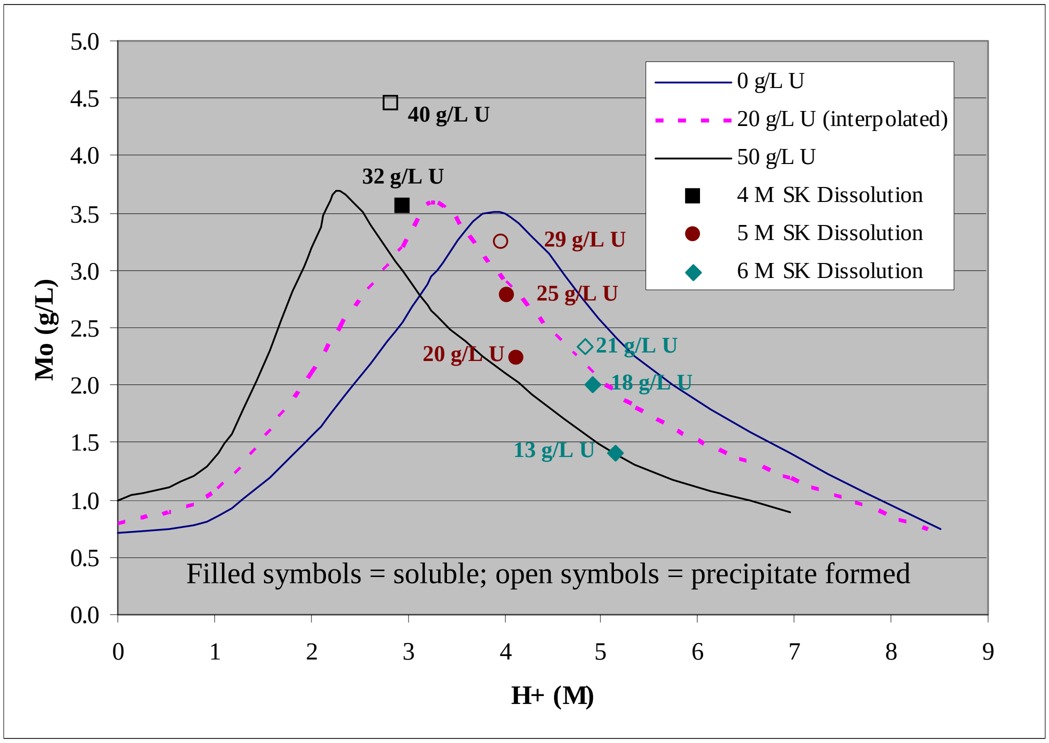

Figure 6. SK Solubility Data vs. Literature Values – 21 Days after Tests

Apart from the inherent uncertainty of the data, Tables 5 and 6 show good agreement with each other and with the expected values of the SK material. The total U-Mo-Ni for ICPMS and ICPES agree with the experimentally weighed and measured values, within method uncertainty, for all but one sample each. The ICPMS U isotopics, within measurement uncertainty, agree with the expected value of 20.034%. For a perfect U/10% Mo material, the ideal U:Mo mole ratio would be 3.64. Within measurement uncertainty, the data of Tables 5 and 6 report the correct U:Mo mole ratio. The presence of Ni in the first four ICPES samples confirms the presence of Ni plating. The ICPES measurements of nominally 1 g/L Fe are consistent with the concentration of Fe added to each experiment, without factoring in evaporative losses. Collectively, the data of Tables 5 and 6 confirm the identity of the SK material and provide a basis for using other U-Mo data in the literature to develop a dissolution flowsheet recommendation.

Gas Generation

Gas generation tests were conducted to supplement the data in the literature. The tests were conducted at 1 M and 2 M HNO_3 because of the understanding that H_2 formation is less favorable at higher acid concentrations. Equations (1)-(5), based on known reactions for Al metal and supported by experimental results, were put forth as an explanation of the acid dependence of H_2 generation during U metal dissolution *(3)*. SRS experience is that Equation (3) best approximates the dissolution of U metal in HNO_3. *(6)*

$$
\begin{array}{l c l r}
 & \uparrow & U + 6HNO_3 \rightarrow UO_2(NO_3)_2 + 3NO_2 + NO + 2H_2O & (1) \\
 & \vert & 2U + 10HNO_3 \rightarrow 2UO_2(NO_3)_2 + 3NO_2 + 3NO + 5H_2O & (2) \\
[HNO_3] & \vert & U + 4.5HNO_3 \rightarrow UO_2(NO_3)_2 + 1.57NO + 0.84NO_2 + & (3) \\
\mathrm{Increase} & \vert & \qquad 0.005N_2O + 0.043N_2 + 2.25\,H_2O & \\
 & \vert & U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO + 2H_2O & (4) \\
 & \vert & 5U + 14HNO_3 \rightarrow 5UO_2(NO_3)_2 + 2N_2O + 7H_2 & (5)
\end{array}
$$

Three consecutive large samples were collected from the test vessel without opening the vessel. For the test in 2 M HNO_3, gas samples of nominally 500 mL, 750 mL and 850 mL were collected in gas sample bags. For the test in 1 M HNO_3, gas samples of nominally 500 mL, 700 mL and 800 mL were collected in gas sample bags. Immediately after the tests, the contents of each bag were exhausted through separate 22-mL gas sample bulbs. Analysis of all six gas sample bulbs showed no detectable H_2 gas. For each sample, the measured H_2 concentration was <0.1 vol%.

The results are consistent with studies in the literature citing very low H_2 generation for U, U-Mo and Mo dissolution in HNO_3. Hydrogen generation for Hallam fuel (U-10Mo) dissolution yielded less than 2 vol% and most of the H_2 can be attributed to the dissolution of Al using Hg catalyst (10). Measurements of off gas during the dissolution of the Piqua (U-3Mo) fuels in H-Canyon yielded a maximum of 0.2 vol% H_2 *(9)*. Hydrogen gas measured from the dissolution of U-3Mo in HNO_3-$Fe(NO_3)_3$ ranged from 0.05-0.20 vol% while U-10Mo showed no detectable H_2 under similar conditions *(5)*. Less than 0.1 vol% H_2 was evolved for U metal dissolution at 100 ^oC in both 4 M HNO_3 and 7 M HNO_3 *(3)*. Molybdenum metal dissolution in 4 M HNO_3 at 90 ^oC found less than 0.1 vol % H_2 in the evolved gases *(4)*. The dissolution of carbon steel, present in the charge bundle end caps and cans, in 2 M HNO_3 with 0.025 M KF and 2 g/L boron at 95 ^oC produced less than 0.1 vol % H_2 *(11)*.

Several observations should be noted. First, the method used for collecting the samples led to each sample being somewhat diluted with air; however, since the dissolution vessel was not opened during each test, the latter samples were less dilute than the first sample. Based on the head space volume and the total volume of gas generated, the third gas sample for each test should have very little residual air. Second, significant evaporation occurred during each test and condensate collected in each sample bag. Because of the moisture, the gas in the bag changed color from yellow-orange to clear as NO_2 absorbed into the condensate, thereby exaggerating the concentration H_2 that might be present. Last, the gas chromatography method used for the H_2 measurement is not sensitive to nitrogen oxide gases. Therefore, the largest fraction of the sample volume cannot be quantified.

RECOMMENDATION

SRNL dissolution testing with Super Kukla material validated the applicability of dissolution and solubility data reported in the literature for various U and U-Mo metals to the SK material. Therefore, adequate data are available to conclude with confidence that the preferred flowsheet for the dissolution of the SK material uses 4.5-5.0 M HNO_3 at 100-105 ^oC to yield a final nominal concentration of 4.0-4.5 M HNO_3, 15-20 g/L U and 1.7-2.2 g/L Mo. The acceptable operating range encompasses a wider starting acid concentration of 3.0-6.0 M HNO_3. Operations above a starting concentration of 6 M HNO_3 have the potential to generate a precipitate that may contain uranium. The acceptable operating range shows no evidence of forming U-Mo solids or of generating a flammable gas mixture.

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