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**SCRAP RECOVERY FOR FABRICATION OF U-10MO FUEL FOR HIGH  
PERFORMANCE REACTORS**

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**ABSTRACT**

Argonne is developing an aqueous-processing flowsheet for scrap recovery in the fuel fabrication process for high-density LEU-monolithic fuel to be used in U.S. high performance research reactors. Significant losses are expected in the fabrication of this fuel, so a means to recycle the scrap pieces is needed. The fuel consists of a monolithic uranium-molybdenum alloy containing 10% (w/w) Mo with Al-alloy cladding and a Zr bonding-layer. Dissolution conditions are currently being investigated that would result in 20 g-U/L and 50 g-U/L solutions without and with Fe(NO<sub>3</sub>)<sub>3</sub> addition to the dissolving solution. HNO<sub>3</sub> and HF concentrations are being optimized for timely dissolution of the fuel scrap and prevention of the formation of the U-Zr<sub>2</sub> intermetallic, explosive complex, while meeting the requirements needed for further processing.

**1. Introduction**

The Global Threat Reduction Initiative is currently engaged in the development of an ultra-high density LEU fuel for its high performance research reactors (HPRRs). The five HPRRs across the US currently use HEU fuel, and nearly 250 kg-U/year are required to operate these reactors.[1] Conversion to a standard LEU aluminide, oxide, or silicide fuel is not feasible because the HPRRs require a higher density of U-235 in the fuel meat than can be afforded by these forms. As a result, a more dense LEU fuel is required to provide the required U-235 densities required for these reactors. A monolithic U-10Mo alloy is an attractive candidate for the fuel meat because it has a density of 15.3 g-U/cm<sup>3</sup>. [1]

U-10Mo foil dissolution experiments were initiated at Argonne to confirm predicted conditions based on recent literature reports describing the aqueous processing of ultra-high density LEU fuels.[2-4] Small-scale experiments generating 20 g-U/L and 50 g-U/L samples were dissolved in solutions with varying HNO<sub>3</sub> concentrations. Molybdenum solubility in the presence of significant amounts of uranium is limited, so the 50 g-U/L samples were dissolved in the presence

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of 0.5 M  $\text{Fe}(\text{NO}_3)_3$ . A negatively charged Fe(III)-molybdate complex forms preventing precipitation of uranyl molybdate.[5-6] Other metal ions are also expected to affect dissolution conditions, i.e., Al and Zr. While aluminum metal is known to dissolve readily in alkaline solutions, it is very slow to dissolve in acid. HF can act as a complexant and is necessary to aid in the single-step dissolution process where the Al cladding is dissolved in the same solution as the U-10Mo fuel meat. To dissolve the Al cladding in less than 6 hours, it has been predicted that a constant concentration of 0.005 M HF is needed.[7] Hydrofluoric acid must also be present in a 4:1 HF:Zr molar ratio to prevent formation of the U-Zr<sub>2</sub> intermetallic complex, which is highly explosive.[4,7] Experiments are being done to verify predicted dissolution conditions and optimize  $\text{HNO}_3$  and HF concentrations for timely dissolution of the fuel without the formation of precipitates, while meeting the requirements needed for further processing by a tributyl-phosphate (TBP) based solvent extraction process to recover uranium from a nitric acid-based media.

Each of the five US high performance research reactors requires slightly different ratios of Al cladding to uranium for the U-10Mo foils. For example, the Missouri University Research Reactor (MURR) requires fuel plates with Al/U molar ratios of 1.9 – 7.7, while the Advanced Test Reactor (ATR) at Idaho National Laboratory (INL) needs fuel plates containing Al/U molar ratios of 4.9 – 24.8.[2] In a previous literature report by Stepinski et. al., the average molar ratio of Al/U based on the number of plates required each year, the plate geometries, and the amount of Al cladding required for the U-10Mo fuels for the National Bureau of Standards Reactor (NBSR) at the National Institute of Standards and Technology (NIST), MURR, and ATR was utilized to predict dissolution conditions.[2] That value assumes a molar ratio of 4.9 Al/U; however, the U-10Mo plates with Al cladding that were obtained from INL contain molar ratios of 18.8 and 111 Al/U.[2] Small-scale experiments are difficult to complete with these types of fuel scrap because 67% and 92% of the fuel mass is Al cladding. Large fuel-scrap pieces would need to be dissolved in small volumes to obtain U concentrations of 20 or 50 g-U/L. In addition, the primary goal of the dissolution experiments was to test predicted conditions, which were based on the fuel having a molar ratio of 4.9 Al/U.

## 2. Experimental

Dissolution experiments were completed to test predicted literature conditions. The dissolution rates, formation of precipitates, and final acid and metal ion concentrations were determined to help optimize conditions needed for further processing. The solutions were heated using a heating mantle or a hot plate (when HF was used). Water and air reflux-condensers were used to prevent loss of the solution through evaporation, and the temperature varied from 95 – 110°C for all dissolutions.

### *U-10Mo Foils*

Dissolution experiments were initiated using U-10Mo foils (no Al cladding or Zr-bonding interlayer) obtained from INL. The U-10Mo foils used in the dissolution experiments contain 89.98% depleted uranium (0.22% U-235) and 10.02% Mo. Smaller pieces of the foil (0.2 – 1.2 g) were cut and dissolved in the appropriate volumes to obtain final uranium concentrations of 20 and 50 g/L. Initial nitric acid concentrations varied from 2 to 6 M, and 0.5 M ferric nitrate was added to samples to contain ~ 50 g-U/L.

#### *U-10Mo Foils with Al Cladding – Single Step Dissolution*

Dissolution conditions were first determined for the Al cladding (Al-6061) by itself in HNO<sub>3</sub> and HF solutions with and without 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub>. Because the foils obtained from INL did not contain Al/U molar ratios of 4.9, a piece of cladding was dissolved first. Immediately after the cladding dissolved, the U-10Mo fuel meat was added to the reaction mixture (89.98% depleted uranium (0.22% U-235) and 10.02% Mo). The final samples contained ~ 20 g-U/L and 50 g-U/L with an Al/U molar ratio of ~ 4.9. Various HNO<sub>3</sub> and HF concentrations were tested.

#### *U-10Mo Foils with Al Cladding and Zr Bonding Layer*

Again, the Al cladding was dissolved by itself, and after it dissolved, a piece of U-10Mo fuel meat with bonded Zr was added to the reaction mixture (83.3% U, 9.3% Mo, and 7.4% Zr). HNO<sub>3</sub> and HF concentrations were varied, and slightly more HF was required to dissolve the cladding and Zr to prevent the formation of the explosive U-Zr<sub>2</sub> complex. Final samples contained ~ 20 and 50 g-U/L with Al/U molar ratios of ~ 4.9.

#### *U-8Mo Foils with Al cladding and Zr Bonding Layer – Two-Step Dissolution*

A two-step process was determined for dissolution of U-8Mo foils with Al cladding and a Zr bonding layer (64.7% Al, 30.5% U, 2.8% Mo, and 2% Zr). The Al cladding was dissolved in a basic solution where the Al/NaOH/NaNO<sub>3</sub> molar ratio was 1/0.85/1.05. After the cladding had dissolved, the basic solution was removed, and the remaining U-8Mo fuel meat was dissolved in a solution containing 5.8 M HNO<sub>3</sub> and a 4:1 molar ratio of HF:Zr with and without Fe(NO<sub>3</sub>)<sub>3</sub>.

#### *Potassium Oxalate Titration*

The final acid concentration was determined using potassium oxalate to complex uranium and other metal ions. A 0.5 mL sample of the dissolved U-10Mo solution was added to 50 mL of a 0.45 M K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution (pH between 5.5 and 5.6). The amount of base (0.1 M NaOH) required to bring the pH back to its initial value was used to calculate the final acid concentration.[8]

#### *Dissolution Rate*

Dissolution rates were determined by measuring the two sides of each piece of foil. The mass of the foil (mg) was divided by the time (time for the foil to dissolve) multiplied by the area of the two sides of the foils (cm<sup>2</sup>).

#### *Inductively Coupled Plasma Mass Spectrometry (ICP-MS)*

Final metal-ion concentrations were determined using ICP-MS, and results are ±10%. Dilutions of the final dissolved foils were made using 0.3 M optima HNO<sub>3</sub>.

### **3 Results**

#### *U-10Mo Foils*

For the 20 g-U/L samples, an orange-red precipitate was observed under all dissolution conditions investigated. However, the small amount of precipitate that forms can easily be dissolved back into solution with a little shaking or sitting at room temperature for 7 – 8 days. A similar precipitate has previously been observed in the dissolution of UO<sub>2</sub> plates in nitric acid that do not contain Mo. Therefore, it is unlikely that the observed precipitate contains Mo. It is possible that a uranium oxide is precipitating out of solution, and uranium trioxide is known to

form from uranyl nitrate solutions at elevated temperatures.[9] However, temperatures of 400°C and greater were not reached under our experimental conditions.

The samples containing 50 g-U/L did not form any precipitates. Ferric nitrate was effective in dissolving larger amounts of Mo in the presence of U without the precipitation of uranyl molybdate. In addition,  $\text{Fe}(\text{NO}_3)_3$  increased dissolution rates 3–4 fold. However, larger nitrate concentrations are expected to lower the solubility of  $\text{Al}(\text{NO}_3)_3$  due to the common-ion effect, but this will be confirmed experimentally when the U-10Mo foils with Al cladding are dissolved.[4]

Conditions have been determined that are reproducible (triplicate) for the dissolution of U-10Mo foils representing a 20 g-U/L solution and a 50 g-U/L solution in the presence of 0.5 M  $\text{Fe}(\text{NO}_3)_3$ . An initial  $\text{HNO}_3$  concentration of 3.4 – 3.5 M for the 20 g-U/L samples and 2.9 - 3.0 M for the 50 g-U/L samples was effective in dissolving the U-10Mo foils with average dissolution rates of 11 and 38 mg/min-cm<sup>2</sup>. Final nitric-acid concentrations of 3 M and 1.8 M are in the range needed for further processing. In a previous report by Stepinski et. al., it suggests that a final  $\text{HNO}_3$  concentration in the range of 2.2 – 5 M is needed for solutions containing 20 g-U/L and 1 – 4 M for solutions containing 50 g-U/L.[4] U-10Mo dissolution results are shown in Table I.

Table I. Results for U-10Mo fuel dissolutions. Final Mo and U concentrations are  $\pm 10\%$ .

Mass (g)	Volume (mL)	Temperature (°C)	U (g)	Mo (g)	Fe (M)	Initial $\text{HNO}_3$ (M)	Final $\text{HNO}_3$ (M)	Dissolution rate (mg/min-cm <sup>2</sup> )	ppt.	Final Mo (g/L)	Final U (g/L)
0.39	17.5	97 - 102	0.35	0.04	0	3.5	3.1	11	yes	2.7	22
0.44	20	95 - 103	0.4	0.044	0	3.4	3	13	yes	2.3	20
1.04	47	92 - 98	0.94	0.1	0	3.4	2.9	8.9	yes	2.2	19
0.52	9.4	93 - 100	0.47	0.05	0.5	3	1.8	29	no	6.3	57
1.14	20.6	96 - 102	1.03	0.11	0.5	2.9	1.8	41	no	5.8	47
1.15	20.6	97 - 104	1.03	0.12	0.5	2.9	1.8	44	no	6.1	51

Several different equations have been cited in the literature for the formation of uranyl nitrate from U metal with molar ratios of  $\text{HNO}_3/\text{U}$  ranging from 2.8 – 6.[10] For the 20 and 50 g-U/L samples, an average molar ratio of 5.2  $\text{HNO}_3/\text{U}$  was obtained, which is within the range reported in the literature. Dissolution of molybdenum will also consume  $\text{HNO}_3$ , which explains why the ratios are at the higher end of the reported range.

Fagueras et al. and Ferris studied the solubility of Mo in the presence of uranyl nitrate, ferric nitrate, and many other metal salts. Based on their data, U-10Mo foils up to 25 g-U/L can be dissolved in  $\geq 3$  M  $\text{HNO}_3$  without precipitation, and in the presence of 0.5 – 1 M  $\text{Fe}(\text{NO}_3)_3$ , up to 90 g-U/L can be dissolved in 2 M  $\text{HNO}_3$  without precipitation.[11,12] Solutions containing ~ 20 g-U/L formed a red-orange precipitate when the initial  $\text{HNO}_3$  was between 3 and 6 M. This contradicts what has been reported and/or predicted based on previous literature reports.[4] However, the precipitate can easily be re-dissolved with a little shaking or time. A larger piece of U-10Mo fuel (1.7 g) was dissolved in an attempt to obtain a more significant amount of

precipitate; however, the amount of precipitate remained too small to collect. For samples containing 50 g-U/L in the presence of 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub>, no precipitation was observed for the entire range of HNO<sub>3</sub> concentrations investigated (2 – 6 M). The results that we obtained for the 50 g-U/L samples with 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub> agree with what has been predicted.

Previous studies have shown that dissolution rates for U-10Mo foils are about 100 mg/min-cm<sup>2</sup> in the presence of 6 M HNO<sub>3</sub> and 2 mg/min-cm<sup>2</sup> in the presence of 2 M HNO<sub>3</sub>. [5,13] The dissolution rates that we observed are within the range expected for initial HNO<sub>3</sub> concentrations of 3.4 – 3.5 M for the 20 g-U/L solutions and 2.9 – 3.0 M for the 50 g-U/L solutions in the presence of 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub>. The average dissolution rates are 11 mg/min-cm<sup>2</sup> for the 20 g-U/L samples and 38 mg/min-cm<sup>2</sup> for the 50 g-U/L samples.

#### *U-10Mo Foils with Al Cladding*

There are two processes suggested for the dissolution of Al-clad fuel. A two-step procedure uses a caustic solution to dissolve the Al cladding, while a single step method utilizes HF to penetrate the aluminum oxide layer, complex the Al, and dissolve the cladding. [2] Results discussed in this report relied solely on the addition of HF to facilitate the single step dissolution. In an effort to test predicted dissolution conditions, a piece of Al cladding was dissolved first, and the remaining amount of U-10Mo fuel meat needed to obtain a 4.9 molar ratio of Al/U was added to the reaction mixture. Again, the purpose of these dissolution experiments was to test predicted conditions and analyze dissolution rates, consumption of HNO<sub>3</sub>, and formation of precipitates.

First, dissolution conditions were determined for the Al cladding by itself in HNO<sub>3</sub> and HF solutions with and without 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub>. The concentration of Al cladding represented what would be required to obtain a 4.9 molar ratio of Al/U for a sample containing 20 g-U/L and 50 g-U/L. It has been suggested that a 1.3 molar ratio of Al/HF would enable appropriate dissolution of the cladding in a single step. [4,7] The Al cladding (~0.45 M in the final solution) was successfully dissolved in a 3.4 M HNO<sub>3</sub> solution containing 0.34 M HF with a dissolution rate of 5.6 mg/min-cm<sup>2</sup>, and no precipitation was observed. However, half of the nitric acid was consumed, so a higher initial nitric acid concentration will be needed to dissolve the U-10Mo fuel with Al cladding and have a final H<sup>+</sup> concentration in the range of 2.2 – 5 M needed for further processing. Dissolution conditions for the Al cladding were also determined in the presence of 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub>. The Al cladding (~1.1 M in the final solution) dissolved in a solution containing 5.8 M HNO<sub>3</sub>, 0.85 M HF, and 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub> with a dissolution rate of 4.3 mg/min-cm<sup>2</sup>. No precipitation was observed. Results for the dissolutions of the Al cladding are given in Table II.

Table II. Results for Al cladding dissolutions. Final Al and Fe concentrations are ± 10%.

Al (g)	Fe (M)	Volume (mL)	Temperature (°C)	Initial HNO <sub>3</sub> (M)	Initial HF (M)	Final H <sup>+</sup> (M)	Final Al (g/L)	Final Fe (g/L)	Cladding Dissolution Rate (mg/min-cm <sup>2</sup> )
0.18	0	14.8	92 - 97	3.4	0.6	1.7	13	0	5.6
0.28	0.5	9.4	93 - 95	5.8	0.85	1.3	29	28	4.3

Three different sets of dissolution experiments were initiated for samples containing final Al/U molar ratios of 4.9, 5.9, and 7.6. For all dissolutions, a piece of Al cladding was dissolved first,

and a U-10Mo foil was added immediately after the cladding dissolved. A small amount of a red-orange precipitate formed as the solution cooled to room temperature. Again, the amount of precipitate was too small to collect on the current scale, but the precipitates re-dissolved within one week. Initial nitric acid concentrations of 3.4 and 5.8 M were tested along with 0.6 and 1 M HF concentrations. The Al cladding and fuel meat dissolution rates increased in the presence of larger amounts of HF. Dissolution conditions were examined using higher concentrations of HF because more HF will be required when Zr is present, and the solubility of Al, U, and Mo in the presence of higher HF concentrations has not been thoroughly investigated. Increasing the HF concentration from 0.6 to 1 M HF did not lead to the formation of larger amounts of precipitates. Again, the red-orange precipitate formed under all three dissolution conditions but was no longer observed after one week. The final H<sup>+</sup> concentration for the last two dissolutions is in the range needed for further processing (2.2 – 5 M).[4] The results for the dissolution experiments with Al cladding and U-10Mo fuel meat added for solutions containing ~ 20 g-U/L are shown in Table III.

Table III. Results for Al cladding with U-10Mo fuel meat dissolutions. Final U, Mo, and Al concentrations are ± 10%.

U (g)	Mo (g)	Al (g)	Vol. (mL)	Temp. (°C)	Initial HNO <sub>3</sub> (M)	Initial HF (M)	Final H <sup>+</sup> (M)	Final U (g/L)	Final Mo (g/L)	Final Al (g/L)	Al/U Molar Ratio	Fuel Meat Dissolution Rate (mg/min-cm <sup>2</sup> )	Cladding Dissolution Rate (mg/min-cm <sup>2</sup> )
0.29	0.029	0.17	15	92 - 98	3.4	0.6	1.4	19	2.2	13	5.9	23	5.8
0.34	0.034	0.18	17	91 - 95	5.8	0.6	3	21	2.5	12	4.9	25	2.4
0.25	0.025	0.19	13	94 - 99	5.8	1	2.8	22	2.4	19	7.6	40	12

Three sets of dissolution experiments were investigated for samples with Al/U molar ratios ranging from 5.1 – 5.5. In the first dissolution experiment, 5.8 M HNO<sub>3</sub> and 1.4 M HF were tested in the presence of 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub>. The cladding dissolved, but after the fuel meat was added, a large amount of red precipitate formed. The U-10Mo foil did not dissolve completely, but the precipitate was collected. ICP-MS results indicate that the sample is mostly Fe (80%) and Mo (12%) with smaller amounts of Al (6%) and U (2%). The higher HF concentration does not work well for dissolving the cladding and fuel meat in the presence of large amounts of Fe. In a second dissolution attempt, after about 4 hours, the Al cladding had not completely dissolved, but the fuel meat was added to the reaction and dissolved within an hour. The Al cladding had still not dissolved but remained in solution at room temperature over the weekend. It dissolved over the weekend, but the solution was a dark orange-red color (all other solutions were yellow). The initial HNO<sub>3</sub> and HF concentrations were 5.8 M and 0.85 M. No precipitates were observed, but ICP-MS results indicate slightly higher metal ion concentrations than expected, U (61 g/L), Mo (6.7 g/L), Al (38 g/L), and Fe ( 31 g/L) In addition, the final H<sup>+</sup> concentration was extremely low ~ 0.1 M, well below the value needed for further processing.[4] In a final dissolution attempt, the Al cladding dissolved with a dissolution rate of 4 mg/min-cm<sup>2</sup>, while the fuel meat dissolved much more rapidly, 75 mg/min-cm<sup>2</sup>. A slightly lower HF concentration was used (0.77 M), and the final acid concentration of 1.1 M was in the necessary range for the TBP extraction process. The solution was yellow, and no precipitates were

observed. ICP-MS values are closer to concentrations expected, U (52 g/L), Mo (6.1 g/L), Al (30 g/L), and Fe (27 g/L). The results are shown in Table IV.

Table IV. Results for Al cladding with U-10Mo fuel meat dissolutions. Final U, Mo, Al, and Fe are  $\pm 10\%$ .

U (g)	Mo (g)	Al (g)	Volume (mL)	Temperature ( $^{\circ}\text{C}$ )	Initial $[\text{HNO}_3]$ (M)	Initial $[\text{HF}]$ (M)	Final $[\text{H}^+]$ (M)	Final U (g/L)	Final Mo (g/L)	Final Al (g/L)	Final Fe (g/L)	Al/U Molar Ratio
0.51	0.051	0.29	10.2	97 - 102	5.8	1.4	5.8	-	-	-	-	-
0.54	0.054	0.3	10.8	93 - 100	5.8	0.85	5.8	61	6.7	38	31	5.5
0.47	0.047	0.27	9.4	99 -106	5.8	0.77	5.8	52	6.1	30	27	5.1

#### *U-10Mo Foils with Al Cladding and Zr Bonding Layer*

The main concern with dissolving the U-10Mo foils with Al cladding and a Zr bonding interlayer is the formation of an intermetallic U-Zr<sub>2</sub> complex, which is highly explosive.[7] Previous studies have shown that the high surface area of the intermetallic phase develops from an unevenly distributed dissolution pattern, and it can be oxidized with explosive potential if its activation energy barrier is overcome.[14,15,16] HF can be added to the reaction mixture to prevent this from occurring; however, HF is also required to aid in the dissolution of the Al cladding. A 4:1 HF/Zr molar ratio has been shown to prevent the formation of this explosive complex.[4,7] The amount of HF that needs to be added is in addition to the amount required to dissolve the Al cladding.

The final small-scale dissolution experiments were initiated for the U-10Mo foils containing Al cladding and a Zr bonding interlayer. Again, a piece of Al cladding was dissolved first followed by a U-10Mo foil containing a Zr bonding layer. For the first set of experiments for the samples containing 20 g-U/L and 50 g-U/L, the Al cladding was dissolved in the presence of 5.8 M HNO<sub>3</sub> and HF at a 1.3 molar ratio Al/HF. After the cladding was dissolved, the fuel meat with Zr was added with the correct amount of HF (4:1 HF/Zr) to fully complex the Zr. In second set of experiments, the amount of HF required for dissolving the cladding and Zr was added at the beginning before the Al cladding had dissolved.

The initial conditions for the dissolutions of samples containing  $\sim 20$  g-U/L and 50 g-U/L are given in Table IV. The first 20 g-U/L sample dissolved fairly quickly with an Al cladding dissolution rate of 9.2 mg/min-cm<sup>2</sup> and fuel meat dissolution rate of 32 mg/min-cm<sup>2</sup>. However, the small amount of red-orange precipitate that was originally observed had re-dissolved within one week. The amount of total HF added was in slight excess to the stoichiometric amounts required for a 1.3 molar ratio of Al/HF and 4:1 molar ratio of HF/Zr. Still, the final H<sup>+</sup> concentration is in the range needed for further processing. No precipitates were observed for the next 20 g-U/L sample, but dissolution rates were lower (5.1 and 11 mg/min-cm<sup>2</sup> for Al cladding and fuel meat) because HF was no longer in excess. The final acid concentration is higher than what would have been expected because less HF was used than in the previous dissolution experiment, and its final H<sup>+</sup> concentration is 4.7 M compared to 3.9 M obtained in the initial dissolution. Unfortunately, the samples containing  $\sim 50$  g-U/L did not perform quite

as well. Precipitation was observed in both dissolution experiments, and ICP-MS results indicate that the makeup of the white precipitate is 23% Al, 21% Fe, 7.5% Zr, 11% Mo, and 37% U. In the second 50 g-U/L dissolution experiment, the fuel meat would not dissolve completely after 4 hours of refluxing. The amount of  $\text{Fe}(\text{NO}_3)_3$  and the larger amounts of HF required make it difficult to find dissolution conditions that keep all metal ions in solution (U, Mo, Al, Zr, and Fe). As a result, a two-step dissolution that removes the Al cladding using a  $\text{NaOH}:\text{NaNO}_3$  solution has been investigated.

Table IV. Initial conditions for Al cladding and U-10Mo with Zr fuel meat dissolutions.

Sample	U (g)	Mo (g)	Zr (g)	Al (g)	Fe (M)	Volume (mL)	Temp. (°C)	Initial $\text{HNO}_3$ (M)	Initial HF (M)	ppt.	Fuel Meat Dissolution Rate (mg/min- $\text{cm}^2$ )	Cladding Dissolution Rate (mg/min- $\text{cm}^2$ )
1	0.25	0.025	0.022	0.15	0	12.5	90 - 97	5.8	0.7	yes	32	9.2
2	0.44	0.044	0.039	0.25	0.5	8.8	93 - 102	5.8	1.1	yes	6.2	3.5
3	0.25	0.025	0.022	0.15	0	12.5	92 - 100	5.8	0.42	no	11	5.1
4	0.43	0.043	0.049	0.26	0.5	8.6	94 - 103	5.8	0.85	yes	-	3.2

Conditions for the one-step dissolution process have been optimized for samples containing ~ 20 g-U/L. Samples containing 50 g-U/L require  $\text{Fe}(\text{NO}_3)_3$ , and all conditions tested produce large amounts of precipitates. As a result, the two-step process is more feasible if dissolver solutions containing higher concentrations of uranium are required, where ferric nitrate is required to prevent precipitation of molybdenum. The final concentrations of all metal ions are shown in Table V.

Table V. Results for U-10Mo with Al cladding and Zr. Final U, Mo, Al, Zr and Fe concentrations are  $\pm 10\%$ .

Sample	Final $\text{H}^+$ (M)	Final U (g/L)	Final Mo (g/L)	Final Al (g/L)	Final Fe (g/L)	Final Zr (g/L)	Final Al/U Molar Ratio (g/L)
1	3.9	21	2.5	12	0	2.1	4.9
2	0.7	55	6.1	31	27	5	5
3	4.7	20	2.3	12	0	1.9	5.3
4	-	-	-	-	-	-	-

#### *U-8Mo Foils with Al cladding and Zr Bonding Layer – Two-Step Dissolution*

A two-step process has been investigated for the dissolution of U-8Mo foils with Al cladding and Zr bonding layer. The Al cladding is first dissolved in a  $\text{NaOH}:\text{NaNO}_3$  solution with an  $\text{Al}/\text{NaOH}/\text{NaNO}_3$  molar ratio of 1/0.85/1.05. The second step is dissolution of the fuel meat in a  $\text{HNO}_3/\text{HF}$  solution with and without  $\text{Fe}(\text{NO}_3)_3$ . Dissolution conditions were optimized for



U-8Mo foils with Al cladding and a Zr bonding layer where the cladding was dissolved in 40 minutes. The basic solution was removed, and the U-8Mo fuel meat with Zr bonding layer was dissolved in a solution containing 5.8 M HNO<sub>3</sub>, 0.2 M HF, and 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub>. The dissolution rate was 2.6 mg/min-cm<sup>2</sup> with a final acid concentration of 1.8 M and a final U concentration of ~ 40 g/L. A sample containing ~ 20 g-U/L with Al cladding (0.45 M) and Zr took a much longer to dissolve with a dissolution rate of 0.99 mg/min-cm<sup>2</sup> and a final acid concentration of 1.7 M.

#### **4 Conclusions**

Conditions have been optimized for the U-10Mo foils with the exception of the red-orange precipitate that forms but re-dissolves in the 20 g-U/L samples. Dissolving a larger U-10Mo foil did not produce a larger amount of precipitate, and the precipitate remained too small to sample.

One-step-dissolution conditions could not be optimized for the U-10Mo foils with Al cladding and Zr representing 50 g-U/L samples in the presence of 0.5 M Fe(NO<sub>3</sub>)<sub>3</sub> without the formation of precipitates. Conditions for the two-step dissolution were determined using U-8Mo foils with Al cladding and Zr bonding interlayer, but the maximum U concentration for timely dissolution (2.5 hours) was 40 g/L.

A more thorough understanding of the HNO<sub>3</sub> consumption when Al cladding and/or Zr are present needs to be obtained. More experiments are planned with U-10Mo foils with Al cladding with and without Zr to obtain consistent, reproducible results for HNO<sub>3</sub> consumption.

Future dissolution experiments will test conditions using varying molar ratios of Al/HF because different results would be expected depending on the ratio. Dissolving the Al cladding takes a significant amount of time in the one-step dissolution process, and foils containing Al/U molar ratios of 24.8 would take a significantly larger amount of time to dissolve compared to foils containing Al/U molar ratios of 1.9. For samples containing larger Al/U ratios, the two-step dissolution process may be more appropriate.

The next step is to develop a full flowsheet for all level operations including U recovery by solvent extraction and reduction to U metal.

#### **5. Acknowledgements**

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## 6 References

- [1] Wachs, D. M., Clark, C. R., Dunavant, R. J., "Conceptual Process Description for the Manufacture of Low-Enriched Uranium-Molybdenum Fuel." INL/EXT-08-13840, February 2008.
- [2] Stepinski, D. C., Swanson, J., Stevens, J. & Vandegrift, G. F. "Dissolution of U-Mo-Alloy Scrap from Fuel Fabrication." June, 2008.
- [3] Stepinski, D. C., Swanson, J., & Vandegrift, G. F. "Dissolution of Irradiated U-Mo Alloy Monolithic Fuel Containing 10% (w/w) Mo." August, 2008.
- [4] Stepinski, C. D., Maggos, L., Swanson, J., Stevens, J., & Vandegrift, G. F. "Scrap Recovery Operations in the Fuel Fabrication Capacity." Proceedings of the Reduced Enrichment for Research and Test Reactors Conference, Washington D. C., USA, October 2008.
- [5] Schulz, W. W. & Duke, E. M. "Reprocessing of Low-Enrichment Uranium-Molybdenum Alloy Fuels." HW-62086, September, 1959.
- [6] Schulz, W. W., Burns, R. E., & Duke, E. M. "Nitric Acid Dissolution of Uranium-Molybdenum Alloy Reactor Fuels." *I&E Proc. Des. Develop.* (1956). **1**, 156.
- [7] Jerden, J., Fortner, J., & Stepinski, D. C. "Dissolution of Zirconium-Bonded, Monolithic, Uranium-Molybdenum Spent Fuel for Uranium Recovery." April, 2009.
- [8] Hofstetter, K. J., Bowers, D. L., & Kemmerlin, R. P. "Determination of the Acidity of Aqueous Solutions Containing Hydrolyzable Metal Ions Using Oxalate Complexation." Barnwell Nuclear Fuel Plant, Barnwell, South Carolina, June, 1978.
- [9] Sheft, I., Fried, S., & Davidson, N. "Preparation of Uranium Trioxide." *J. Am. Chem. Soc.* (1950). **72**, 2172-2173.
- [10] Pierce, R. A. "Uranium Metal Dissolution in the Presence of Fluoride and Boron." WSRC-TR-2003-0500, November, 2003.
- [11] Faugeras, P., Lheureux, C., & Leroy, P. "Etude De Solubilité Du Molybdène en Milieu Nitrique." CEA Report No. 1823, Nuclear Study Center, Seclay, France, 1961.
- [12] Ferris, L.M. "Solubility of Molybdic Oxide and Its Hydrates in Nitric Acid-Ferric Nitrate and Nitric Acid-Uranyl Nitrate Solutions." *J. Chem. Eng. Data.* (1961). **6**, 600.
- [13] Ferris, L. M. "Aqueous Processing For Dissolution of Uranium-Molybdenum Alloy Reactor Fuel Elements." ORNL-3068. July, 1961.
- [14] Gens, T. A. "Explosive Reactions During Reprocessing of Reactor Fuels Containing Uranium and Zirconium or Niobium." Oak Ridge National Laboratory report: CF-58-11-31, November, 1958.
- [15] Swanson, J. L., "An Estimation of the Explosion Hazard During Reprocessing of Metallic Uranium Fuel Elements Metallurgically Bonded to Zircaloy Cladding." Hanford Report: HW-62109, September, 1959.
- [16] Jackson, R. J., and Johns, W. L. "Explosive Nature of Uranium-Base Niobium Alloys After Immersion in Nitric Acid." Dow Chemical Company, Rocky Flats Division Report: RFP-1575, December, 1970.