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GTRI PROGRESS IN TECHNOLOGY DEVELOPMENT FOR CONVERSION OF ^{99}MO PRODUCTION TO LOW ENRICHED URANIUM

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ABSTRACT

The Global Threat Reduction Initiative (GTRI)--Reactor Conversion program supports the conversion of domestic and international civilian research reactors and isotope production facilities from the use of high enriched uranium (HEU) to low enriched uranium (LEU) fuel and targets. The main technology components of the program are: (1) the development of advanced LEU fuels, (2) design and safety analysis for research reactor conversion, and (3) development of targets and processes for the production of ^{99}Mo without using HEU. For the last technology component, GTRI makes technical expertise available, on a non-proprietary basis, to global medical-isotope producers to assist with converting their ^{99}Mo processes to use LEU and provides technical support in a number of areas, including foil rolling, target fabrication, target irradiation, target disassembly, target dissolution, product recovery and purification, and waste treatment. Argonne continues to support the conversion of international ^{99}Mo production by (1) developing front-end processes that will allow the use of high density-LEU-foil targets to be used in the alkaline processes being used in the production of ^{99}Mo using HEU targets by the current producers, (2) cooperating with ICN and Y-12 to perform LEU-foil-target qualification experiments in Pitesti, Romania, , and (3) working with the IAEA Working Group for Conversion Planning for ^{99}Mo Production Facilities from HEU to LEU.

1. Introduction

The Global Threat Reduction Initiative (GTRI)--Conversion Program develops technology necessary to enable the conversion of civilian facilities using high enriched uranium (HEU) to low enriched uranium (LEU) fuels and targets. The conversion of conventional HEU dispersion targets to LEU for the production of ^{99}Mo production requires approximately five-times the uranium in a target to maintain the ^{99}Mo yield per target. Under GTRI, Argonne National Laboratory is involved in three activities that support conversion of current Mo producers from HEU to LEU targets.

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The first activity is developing two frontend options to the current processes to allow the use of LEU-foil targets. Because of the high density of uranium in uranium-metal foils compared to that in dispersion-fuel meats, these LEU foil targets will allow equal or greater ^{99}Mo production then is now produced with HEU-dispersion targets. Both the frontend-process options under development have two major goals. The first goal is to produce a Mo-product solution from the LEU-foil frontend that will be compatible with current purification operations and that will, with the same number of targets irradiated, provide the same or higher yield of ^{99}Mo at the end of processing. The second goal is to deliver a product solution that is of the same or higher Mo purity than the current solution and is of equal or better compatibility with current purification process.

In the first frontend option, the LEU foil (contained in a thin (10-15 µm) Ni fission-recoil barrier is removed from the annular target and dissolved in nitric acid. In the dissolution, the uranium, nickel, and all fission and activation products are dissolved. The resultant solution (~0.5L) will be ~7 mM Mo, ~450 g-U/L, and the nitric-acid concentration after dissolution will be ~1 M. After dissolution, the solution will be feed to a small column of titania sorbent, where Mo will be sorbed on the column with minor amounts of other feed components. The column will be washed with nitric acid and then water; then Mo will be stripped into a sodium hydroxide solution. In the second option, the LEU-foil target uses a 40-µm aluminum fission recoil barrier. Once the Al/U foil is removed from the target, the Al layer is dissolved in base to expose the uranium surface. This is followed by a low-temperature, low-pressure procedure employing anodic oxidation of the uranium metal into an aqueous bicarbonate solution. After precipitation of uranium, carbonate, and alkaline-insoluble fission and activation products from the solution by the addition of calcium oxide, the Mo solution can be fed into the current purification processes.

The second activity is cooperating with Y-12 and ICN to perform a series of irradiations and post-irradiation examination (PIE) of LEU-foil targets in Pitesti Romania to the collect data necessary to qualify the LEU-foil target for the producers to irradiate these targets in reactors they currently use for their HEU targets. In this cooperation, Y-12 will fabricate the annular LEU-foil targets, and ICN will irradiate in their 14-MW TRIGA reactor and perform PIE in their hot-cell facility over a twelve-month period. Argonne will coordinate activities and provide technical support. This project should be starting in the fall of 2011.

The third Argonne activity is participation in the IAEA Working Group for Conversion Planning for Molybdenum-99 (Mo-99) Production Facilities from Highly Enriched Uranium (HEU) to Low Enriched Uranium (LEU). December 1-2 2011, Argonne will host the working group and give them an update on our progress, including laboratory tours.

The remainder of this paper will discuss progress on activity 1.

2. Development of an Ambient Pressure, Nitric-Acid-Dissolver System for LEU Foils

A nitric-acid-dissolver system was designed to allow the dissolution of up to 250 grams of irradiated uranium foil and associated Ni fission-recoil barrier at ambient pressure. Components of the dissolver system are currently being tested so that the design can be optimized in preparation for a full-scale demonstration. The key design criteria that this dissolver system must incorporate are listed below.

- All water vapor, reaction products, and fission gases must be contained within the dissolver system at a maximum temperature of 125°C and 2 atmospheres of pressure (absolute) under both normal and off-normal (loss of cooling during reaction) conditions.
- The acid feed system must be designed so that the thermally hot LEU foil (hot from decay heat) can be immersed in nitric acid without losing solution due to instantaneous boiling.
- All dissolver system components must designed for remote operation in a hot cell facility.
- Gas-trap components must be designed to trap/neutralize all nitrogen oxide and acid gases (NO, NO_2, HNO_2, HNO_3) as well as trap iodine gas for possible extraction of economically important iodine isotopes (noble fission gases will be passively contained).

Dissolution Reaction and Off-gas Composition

The volume and concentration of nitric acid for a given experiment will depend on the mass of the metal being dissolved as well as the desired final acid concentration of the "product" solution. Controlling the final acid concentration is important for optimizing the ^{99}Mo recovery step follows dissolution. The volumes and concentrations of acid as well as the amount of nitrogen oxide gas that will be produced are determined by the following general reaction:

$$U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_2O + 2NO(g).$$

In the presence of oxygen, the NO(g) produced in these dissolution reactions is rapidly converted to $NO_2(g)$:

$$NO + 0.5O_2 \rightarrow NO_2.$$

Using the kinetic rate law presented by Chilton, one finds that the rate of the $NO \rightarrow NO_2$ reaction is on the order of milliseconds to seconds even at relatively low O_2 partial pressures (0.1 – 0.001 atm).[1] When water vapor and oxygen are present, NO_2 can be converted to both nitrous and nitric acid vapors which will dissolve in condensed water and flow back down into the dissolver. In an effort to be more precise about the concentrations of off-gas species, relative amounts of the important nitrogen oxide gases produced by the dissolution of different amounts of LEU were calculated using the thermodynamic code OLI-ESP. These calculations predict that approximately 2.1 moles of $NO_x + H_2O_{(g)}$ will be present in the dissolver following the dissolution of 250 grams of LEU foil. These results provide a design basis for the off-gas treatment components of the dissolver system.[2]

Most of the off gas from the dissolver will consist of the NO_x;[2] however, ORIGIN calculations show that iodine, xenon, and krypton will also be present in the off-gas. The ORIGIN calculations, performed by Charlie Allen, University of Missouri, using ORIGEN2, Version 2.2, assume the following: Irradiation of 1 gram of uranium foil enriched to 19.75% ^{235}U, Power = 1.9E-3 megawatts, Burnup = 1.59E-2 megawatt days, Flux = 2.1E14 N/cm^2 sec, Burnup is for 200 hours, foil composition is given for cooling times of 12, 24, 36 and 48 hours. After 12-hour cooling, the most abundant off-gas species for 250 g of LEU will be iodine (4.2×10^4 Ci), xenon (2.6×10^4 Ci), and krypton (1.7×10^3 Ci) As part of this study the feasibility of using copper metal to trap and extract iodine gas from the dissolver during the dissolution reaction has been assessed experimentally. The efficiency of NaOH to neutralize/trap the NOx gases has also been investigated.

Reaction Heat and Decay Heat

Thermodynamic calculations show that the dissolution of 250 grams uranium metal (~1.05 moles) the total energy released may be up to 1600 kJ, but will probably be closer to 1000 kJ. Assuming adiabatic conditions and a 30 minute reaction time this energy would correspond to a maximum thermal power output of approximately 890 watts. It has been noted in previous uranium metal dissolution experiments performed at Argonne that there can be a thermal spike during dissolution that involves the relatively sudden release of heat (within a few minutes).[3] Dissolution experiments are planned to test if this sudden heat output also occurs in the new larger, better mixed dissolver. The ORIGEN calculations show that a total thermal output for 250 g of irradiated LEU is around 1000 watts after 12-hour cooling.

Based on the enthalpy and decay heat calculations, the cooling system for the dissolver system must be able to sink out a maximum of 2000 watts (thermal). Therefore, if it is assumed that the dissolution if 250 g of irradiated LEU foil takes 30 minutes, 2000 watts of thermal power will be generated and will need to be removed from the system to ensure that water vapor (and acid) is not lost during the dissolution process. Experiments in which both the reaction and decay heats are simulated using heating coils wrapped around the dissolver vessel are underway to test the performance of the dissolver cooling system.

Dissolver Design Overview

The nitric acid LEU foil dissolver is designed to operate at pressures less than 2 atmospheres (absolute) and at temperatures less than 125^{o}C. A flow diagram of the component sections of the nitric acid dissolver and Mo-99 extraction process is shown in Figure 1. The design concept of the dissolver is shown in Figure 2 and 3.

The dissolver system consists of a 304 stainless steel vessel (2 liter volume) connected to an approximately 65 liter (30cm x 90cm) off-gas reservoir. The dissolver vessel is open to the off-gas reservoir during the dissolution process. The volume of the reservoir was chosen to provide passive containment of all water vapor and reaction products at a pressure less than 2 atmospheres (absolute), during both normal and off-normal (loss of cooling during reaction) conditions. In order to keep the temperature of the gas within the reservoir to below 100^{o}C during a potential loss of cooling, the reservoir is clad in an aluminum heat sink (Al fin rings).

The dissolution process is started by first lowering the uranium foil (contained within a steel mesh basket) into the dissolver vessel and then sealing the vessel with a metal cap. Pre-heated acid (~100^{o}C) is then added to the vessel using a two chamber acid feed system that is designed to avoid pressurization of the acid bottle in the event that the dissolution reaction begins instantaneously when the acid addition step is started. The dissolver vessel is cooled by forced air blown from the base of the unit. The temperature of the dissolver solution is monitored by a thermocouple. The dissolver vessel is insulated so that the top of the vessel is cooled continuously during the reaction. Heat loss from the top of the vessel is optimized by the presence of steel cooling fins attached to the condenser part of the dissolver system. This design causes the water vapor to condense along the walls at the top of the vessel during the dissolution reaction (as acid is boiling); this process is shown schematically in Figure 3. The experimental set-up of the dissolver vessel and condenser section that is being used to test the dissolver/condenser performance is shown in Figure 4.

Summary of Results and Future Plans

The key design criteria were addressed experimentally to optimize the components of the LEU-foil nitric-acid dissolver. Results from ongoing and future tests will be used to finalize the design and fabricate all parts in preparation for a full scale demonstration. The design criteria that have been investigated by ongoing experiments are as follows:

- Preliminary "shakedown" tests of the dissolver vessel, condenser section, and cooling air blower suggest that all water vapor, reaction products and fission gases will be contained within the dissolver system at a maximum temperature of 125^{o}C and 2 atmospheres (absolute) under both normal and off normal (loss of cooling during reaction) conditions. However, more experimental work is needed to confirm and quantify this observation.
- A two-chamber acid delivery system was tested, and the initial results indicate that the design is capable of delivering nitric acid to thermally hot LEU foils (hot due to decay heat) without losing acid due to sudden boiling. The acid delivery component is also designed for remote operation in a hot cell facility.
- Preliminary feasibility tests show that the copper metal trap for iodine sequestration and recovery has promise. The NaOH NO_x trap is a proven technology; however, we continue to work on dissolver system designs that most efficiently incorporate the NO_x trap into the overall design.

Our future plans are to continue the heat-flow testing of the dissolver cooling components; ongoing tests will "map" the thermal gradients both inside and outside the dissolver so that the condenser section design can be optimized. Then, dissolution experiments on uranium foils will be performed to test the cooling system/condenser performance in the presence of different amounts of uranium. This will allow us to quantify how the exothermic heat output from the dissolving uranium foil affects the cooling system performance. These tests will also allow testing of the gas-traps and off-gas reservoir. At this point, all components will be tested in a manipulator mock-up facility to ensure that the dissolver system can be used at a production scale in a hot cell facility.

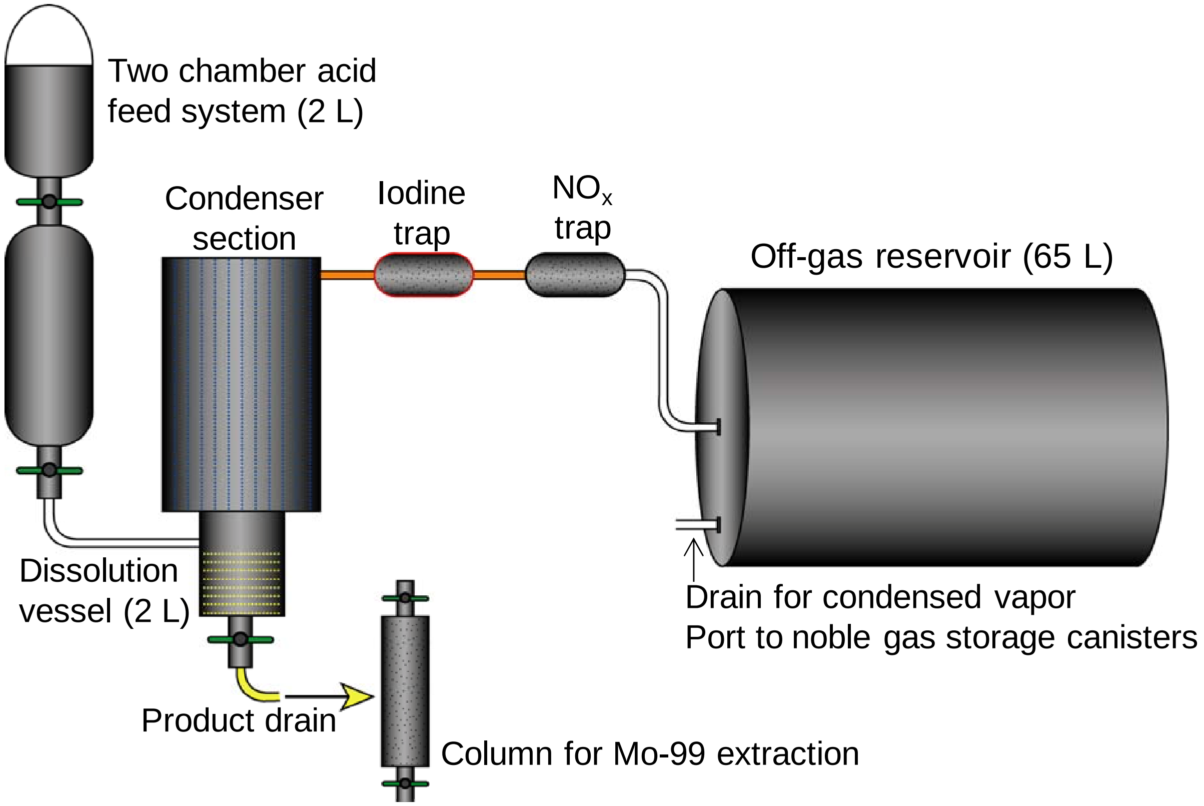

Figure 1. Flow diagram of components of the dissolver system and the ^{99}Mo-extraction column.

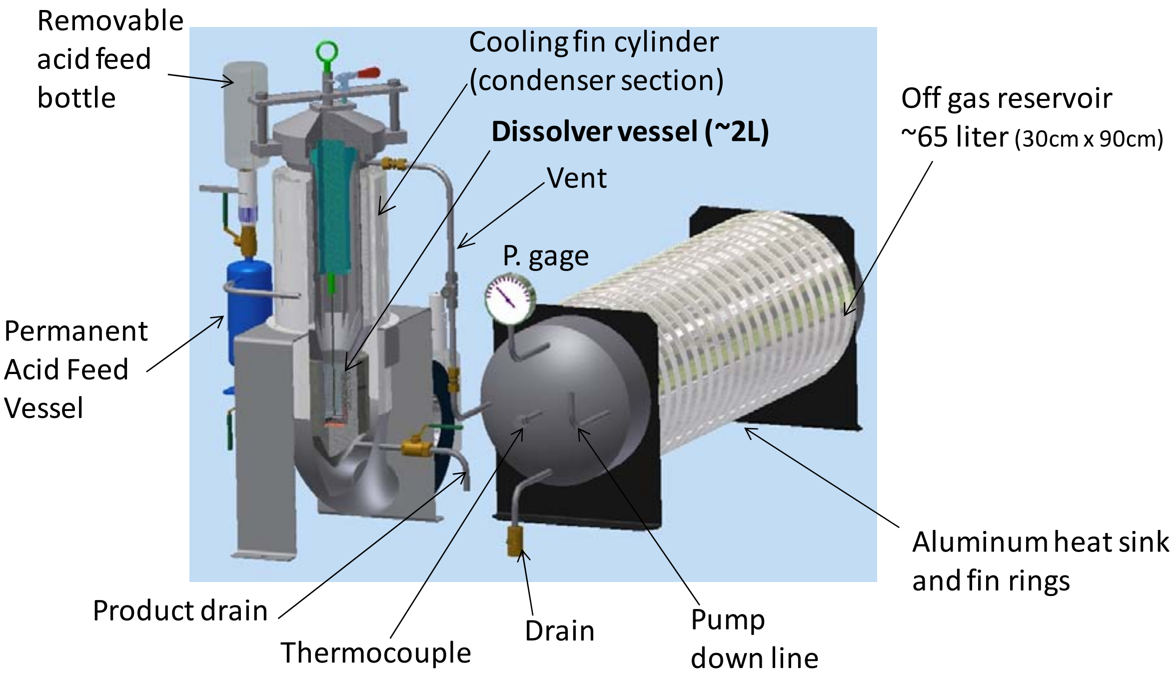

Figure 2. Conceptual drawing of the nitric-acid dissolver system.

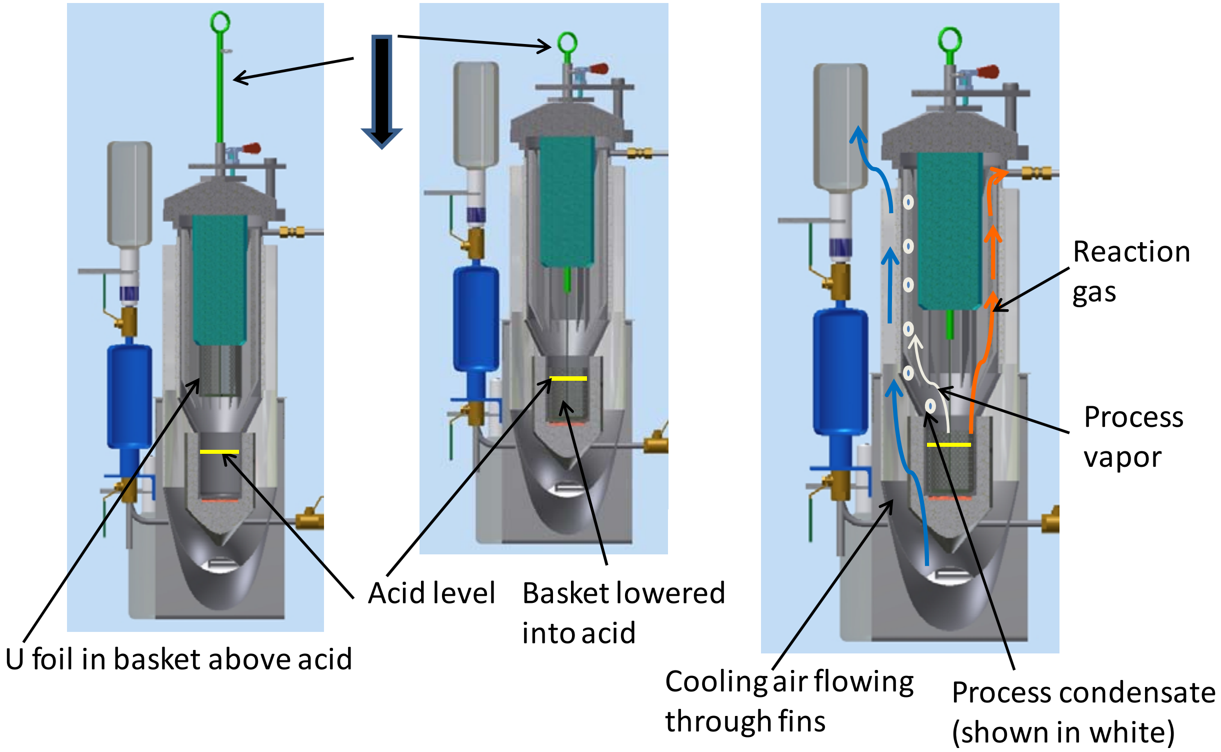

Figure 3. Conceptual drawing of the nitric-acid dissolver system showing the steps involved in starting the dissolution and gas flows during operation.

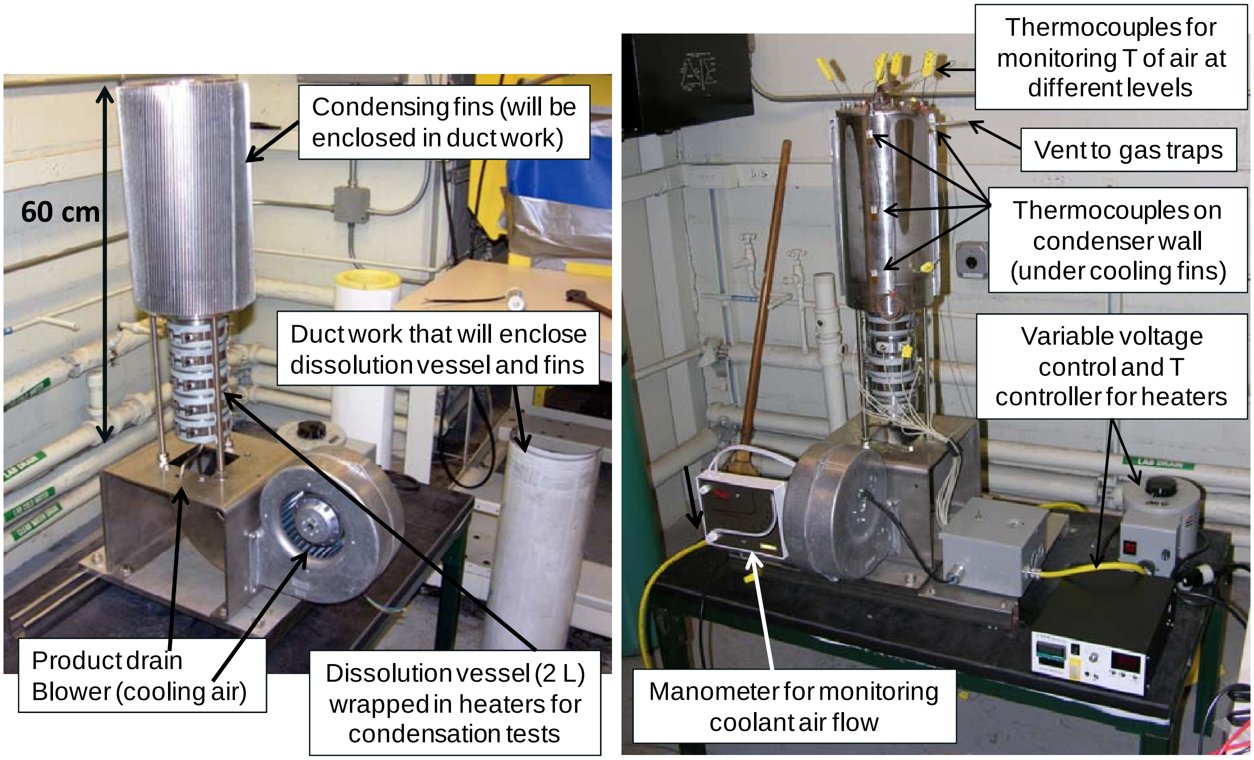

Figure 4. Dissolver used in initial tests: picture on left shows dissolver vessel and condenser section. On the right is a picture of the dissolver during set-up for condenser tests showing the array of thermocouples used to monitor heat gradients inside and outside the dissolver.

3. Recovery of Mo from the Nitric-Acid Dissolver Solution

Titania based sorbents have been identified as supports for separation of Mo from concentrated uranium solutions. They offer high capacity, remarkable K_d values, and are slightly affected by the presence of uranium. Their superior performance in the presence of high concentrations of uranium contrasts alumina. The Mo K_d for alumina decreases dramatically in the presence of high concentrations of uranium, making it unsuitable for recovery of Mo from highly concentrated uranium solutions.

Adsorption of metal ions on inorganic supports such as alumina or titania is often slow and tends to take several hours or days to reach equilibrium in batch contacts. Slow adsorption kinetics relative to mass transfer rates lead to slow development of constant mass transfer pattern. Non-equilibrium adsorption/desorption can introduce large errors to column designs, sorbent capacity, and estimation of system parameters. In this study, a non-constant pattern mass-transfer-zone (NCP-MTZ) method was applied to the design and optimization of Mo separation using a titania column. In this approach, batch tests were conducted to estimate isotherm parameters, and breakthrough column experiments were utilized to determine particle diffusivity (D_p) for each sorbent. Once the intrinsic parameters were determined, VERSE (Versatile Reaction and Separation—developed by Purdue University, IN, USA) simulations were carried out to estimate mass transfer zone (MTZ) at various linear velocities and loading times. Determination of MTZ lengths allows design of process separation column. Key designs were verified experimentally, through loading and breakthrough experiments, to verify D_p, MTZ, and column designs.

Estimation of the effective isotherm parameters of Mo

TiO_2 (80 µm) and Al_2O_3 (75-150 µm) were evaluated for recovery of Mo from uranyl nitrate solutions containing 450 g-U/L and 1 M HNO_3--Figure 5. The data from batch equilibrium experiments were used to estimate the effective Mo isotherm parameters for TiO_2 sorbent. All batch equilibrium data were equilibrated for 24 hours at 60°C. Mo capacity at this feed concentration (q_{Cf}) is five-times higher for titania sorbent than alumina, indicating the need for a five-fold larger alumina-based column.

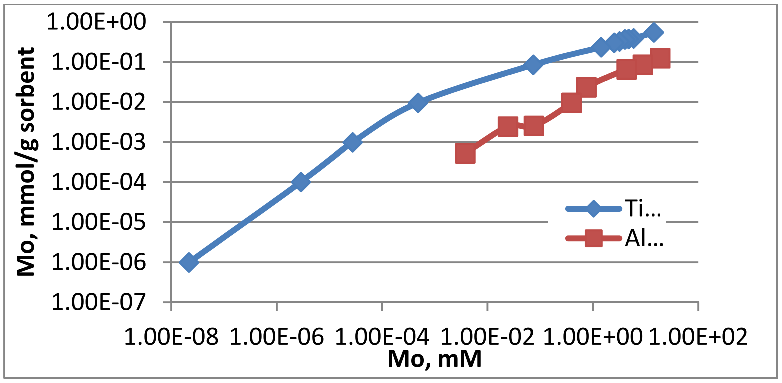

Figure 5. Uptake of molybdenum on alumina and titania from 450 gU/L, 1 M HNO_3 solutions

The Langmuir model was tested for the sorption of Mo in this study:

$$q_i = \frac{a_i C_{p,i}}{1 + \sum_{j=1}^{N} b_j C_{p,j}}$$

where q_i is the amount of species i sorbed on the column packing and equilibrated with the concentration in mobile phase, $C_{p,i}$. In this study, both q_i (meq/L) and $C_{p,i}$ (mol/L) of the Mo isotherm is described on volume basis assuming 1.3 g/mL dry packing density of TiO_2 sorbent. Experimental data and the model predictions are shown in figure 6.

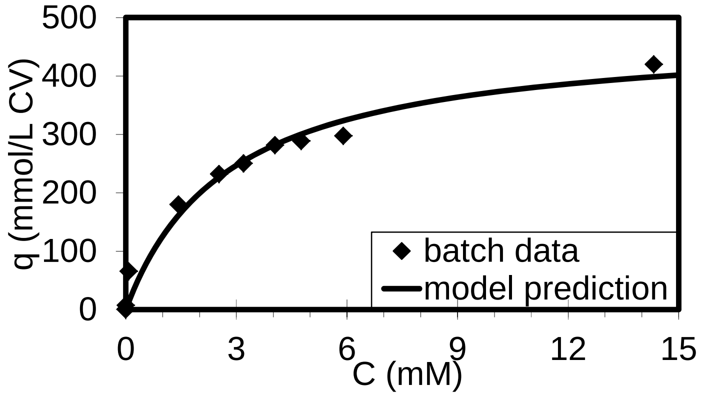

Figure 6. Comparison of isotherm data from batch tests and Langmuir isotherm model prediction for uptake of Mo on the titania sorbent.

The linear isotherm parameter "*a*" was estimated from the data in the low Mo concentration range ([Mo] ≤ 10^{-3} mM). The nonlinear isotherm parameter "*b*" was estimated by minimizing the sum of the relative errors $[\Sigma\left(\frac{q-q'}{q}\right)^2]$ between the experimental (q) and the predicted (q'').

The calculated Langmuir isotherm model parameter a = 171.22, b = 0.36 mM^{-1} and q_{max} = 476 mmol/LCV for adsorption of Mo on titania sorbent. When C = 7 mM, q_C = 340.66 mmol/LCV.

Estimation of other mass transfer parameters of Mo

The axial dispersion coefficient, E_b, was estimated using the Chung and Wen correlation.[4] The mass transfer coefficient, k_f, was estimated using the Wilson and Geankoplis correlation.[5] Brownian diffusivity (D_∞) values of $HMoO_4^-$ in aqueous solution at 25°C used in the simulations were reported to be 8.3 cm^2/min.[6] The Stokes-Einstein equation was then used to correct the D_∞ for solution viscosity and temperature effects. At 60°C, the viscosity of 450 gU/L $UO_2(NO_3)_2$ and 1 M HNO_3 was calculated to be 1.40 cp, using a correlation listed in HW-57386.[7]. Therefore, at 60°C, $D_{\infty,Mo}$ in 450 gU/L $UO_2(NO_3)_2$ and 1 M HNO_3 solution was estimated to be 5.85 × 10^{-4} cm^2/min.

Estimation of the intraparticle diffusivity values (D_p) of Mo from breakthrough curves

Two breakthrough experiments, at 7 mM Mo in 450 gU/L, 1 M HNO_3, were run to estimate D_p and Mo capacity from breakthrough curves (Figure 7 a and b).

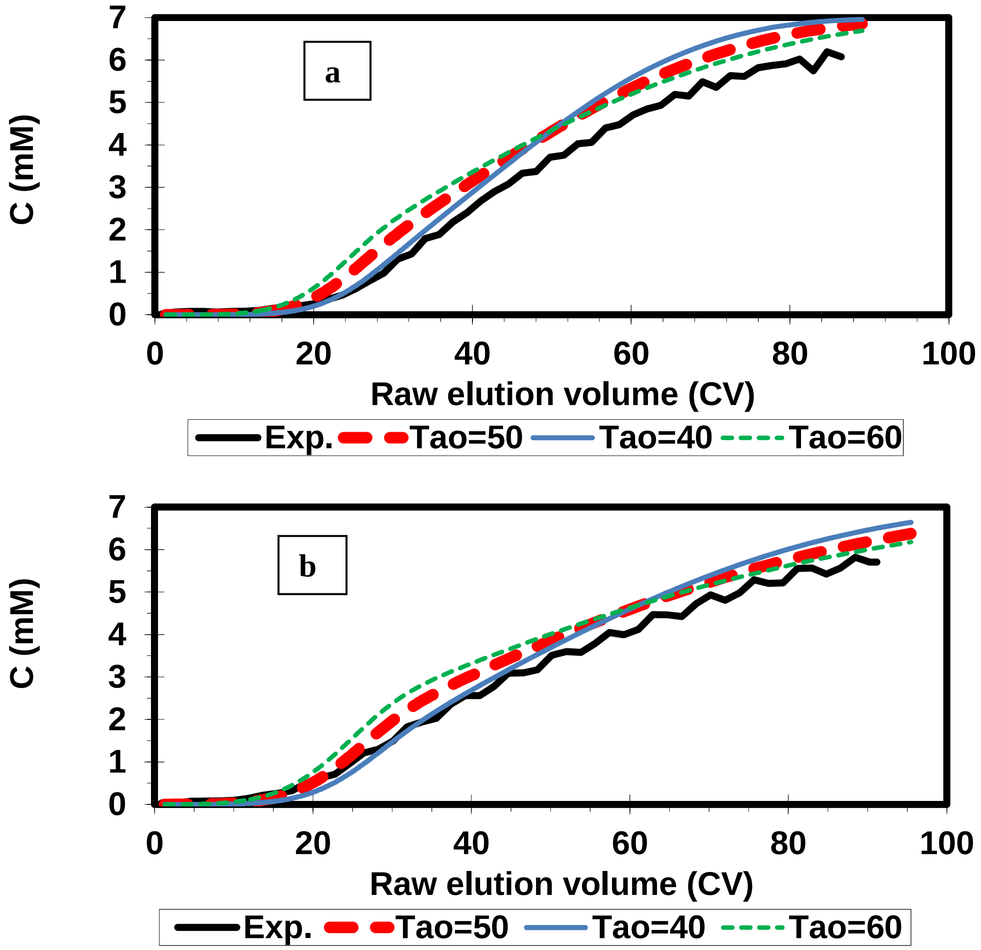

Figure 7(a and b). Breakthrough experiments and D_p estimation for Mo.

In the first experiment, the breakthrough curve was obtained by loading 110 mL of feed solution onto a 6.6 x 32 mm column at 5 cm/min. The second breakthrough curve was obtained by loading 135 mL of feed onto a 6.6 x 42 mm column at 9 cm/min.

Mo capacity from breakthrough experiments was estimated using the equation

$$q\ at\ C = C \times \left(\frac{V_{br}}{CV} - \varepsilon_t - \frac{DV_{sys}}{CV} - \frac{DV_{cap}}{CV}\right)$$

where C is Mo concentration in feed solution (mM), V_{br} is the raw breakthrough volume (mL), q is amount of Mo adsorbed per packing volume of sorbent (mmol/L CV), CV is column volume (mL), ε_t is total column void fraction (assume ε_t = 0.77 for TiO_2), DV is the dead volume in the system; for system (subscript sys) or for column caps/adjusters (subscript cap).

Capacity at feed concentration (q_{Cf})was determined to be 326 and 336 mmol/LCV, respectively. The capacity estimated from breakthrough experiments is within 5% of the q_{Cf} determined from batch experiments.

The intraparticle diffusivity was estimated by comparing the experimental Mo breakthrough curves with VERSE simulations (Figure 7 a and b). In 450 g-U/L $UO_2(NO_3)_2$ and 1 M HNO_3 solution, the intraparticle diffusivities of Mo on TiO_2, assuming $D_\infty/D_p = 50$ (Tao in Figure 7), is estimated to be $D_p = 1.17 \times 10^{-5}$ cm^2/min. Intraparticle diffusion of Mo is assumed to be pore diffusion. As shown in a recent paper of Chung et al. (2010), in a linear isotherm range, surface diffusion effects cannot be distinguished from pore diffusion effects, and, therefore, an effective pore diffusion coefficient is sufficient to take into account of pore diffusion, surface diffusion, or parallel pore diffusion.[8]

The agreement between experimental Mo breakthrough curves and model prediction in 450 gU/L $UO_2(NO_3)_2$ and 1 M HNO_3 indicates that (a) the adsorption of Mo can be described by the effective Langmuir isotherm, and (b) the numerical parameters and the intrinsic model parameters (including void fractions, isotherm, and mass transfer parameters) are sufficiently accurate to predict the Mo breakthrough curves.

Column Designs for Mo Recovery

VERSE simulations were carried out to estimate mass transfer zone (MTZ) at various linear velocities and loading times. Determination of MTZ lengths allowed design of separation processes at various column IDs and velocities. The Mo recovery processes aim to: (1) load 500 mL of 7 mM Mo, 450 gU/L uranyl nitrate and 1 M HNO_3, (2) recover (a) 99% of Mo (b) 99.9%Mo from the feed, and (3) keep pressure drop of the column to be less than 0.8 atm. Column designs for loading 99 % of Mo are listed in Table 1, and for loading 99.9% Mo are listed in Table 2.

Table 1. Possible column designs for 99.0% Mo recovery

u_s (cm/min)	*ID* (cm)	$t_{Loading}$ (min)	$L_{1\%Cf}$ (cm)	When $L_{min} \geq 2\ L_{1\%Cf}$			
				L_{min} (cm)	CV_{min} (mL)	$W_{sorbent}$ (g)	ΔP (atm)
3	4.0	13.26	2.5	5	63	82	0.1
3	3.0	23.58	3.4	7	50	64	0.1
3	2.5	33.95	4.2	9	44	57	0.2
3	2.0	53.05	5.5	11	35	45	0.2
3	1.5	94.31	8.2	16	28	37	0.3
5	3.0	14.15	3.1	6	42	55	0.2
5	2.0	31.83	4.9	10	31	41	0.3
5	1.5	56.59	7.0	14	25	32	0.5
9	3.0	7.86	6.3	12	85	110	0.7

Table 2. Column designs for 99.9% Mo recovery

u_s (cm/min)	ID (cm)	$t_{Loading}$ (min)	$L_{0.1\%Cf}$ (cm)	When $L_{min} \geq 2\ L_{1\%Cf}$			
				$2L_{min}$ (cm)	CV_{min} (mL)	$W_{sorbent}$ (g)	ΔP (atm)
3	4.0	13.26	3.1	6	75	98	0.1
3	3.0	23.58	4.1	8	57	74	0.2
3	2.5	33.95	5.0	10	49	64	0.2
3	2.0	53.05	6.4	13	41	53	0.3
3	1.5	94.31	9.1	18	32	41	0.4
5	3.0	14.15	3.8	8	57	74	0.3
5	2.0	31.83	5.8	12	38	49	0.4
5	1.5	56.59	8.0	16	28	37	0.5

Experimental Verification of Lab-scale Mo Recovery Process

Experiments were carried out to test the column designs reported in Table 1 and 2, with the inner diameter scaled down to 6.6 mm . The percent Mo loading are listed in Table 3. The verification of column designs for loading 99% of Mo was successful, but the longer columns for 99.9% loading did not meet the goal and, in fact, had less capacity than the shorter columns, which is contrary to all theory. The longer-column experiment will be repeated. Overall, however, the results of experimental verification of column designs indicate that the NCP-MTZ method is a precise and highly efficient approach to design of column processes for Mo recovery.

Table 3. Results of experimental verification of column designs.

u_s (cm/min)	ID (cm)	L_{min} (cm)	$t_{Loading}$ (min)	V_{feed} (mL)	target Mo loading (%)	Mo loading (%)
3	0.66	7.5	23.58	28	99	99.1
5	0.66	6.2	14.15	25	99	99.0
5	0.66	10	31.83	56	99	98.7
5	0.66	10	56.59	97	99	98.8
3	0.66	10	33.95	35	99.9	86.8
5	0.66	12	31.83	55	99.9	94.1

Recovery of Mo from TiO_2 columns

Full recovery of Mo can be achieved by counter-current stripping using 0.1 M NaOH. The Mo recovery for counter-current striping with 0.1 M NaOH was between 88-105 ± 5%, with an average 95.3 ± 5%, Table 4. Figure 8 shows the stripping curves for breakthrough and loading experiments performed with solution containing 7 mM Mo, 450 gU/L and 1 M HNO_3. The resulting stripping curves demonstrate that Mo can be qualitatively stripped from titania sorbent at 3 and 5 cm/min linear velocities. The different stripping curve areas are reflected in the %Mo sorbent loading relative to sorbent capacity at feed concentration (q_{Cf}) as specified in Table 5. The results indicate that Mo can be stripped within 15 bed volumes, or, depending on design, 600-900 mL of 0.1 M NaOH (process scale column).

Table 4. Results of column stripping with 0.1 M NaOH

stripping u_s (cm/min)	*ID* (cm)	L_{min} (cm)	Sorbent loading, %q_{Cf}	Mo recovery (%)
5	0.66	6.2	16.1	93.5
3	0.66	7.5	95.2	88.4
5	0.66	10	40.3	97.4
5	0.66	12	17.7	93.9
3	0.66	10	11.7	95.0
5	0.66	3.2	78.6	104
5	0.66	4.2	79.0	105

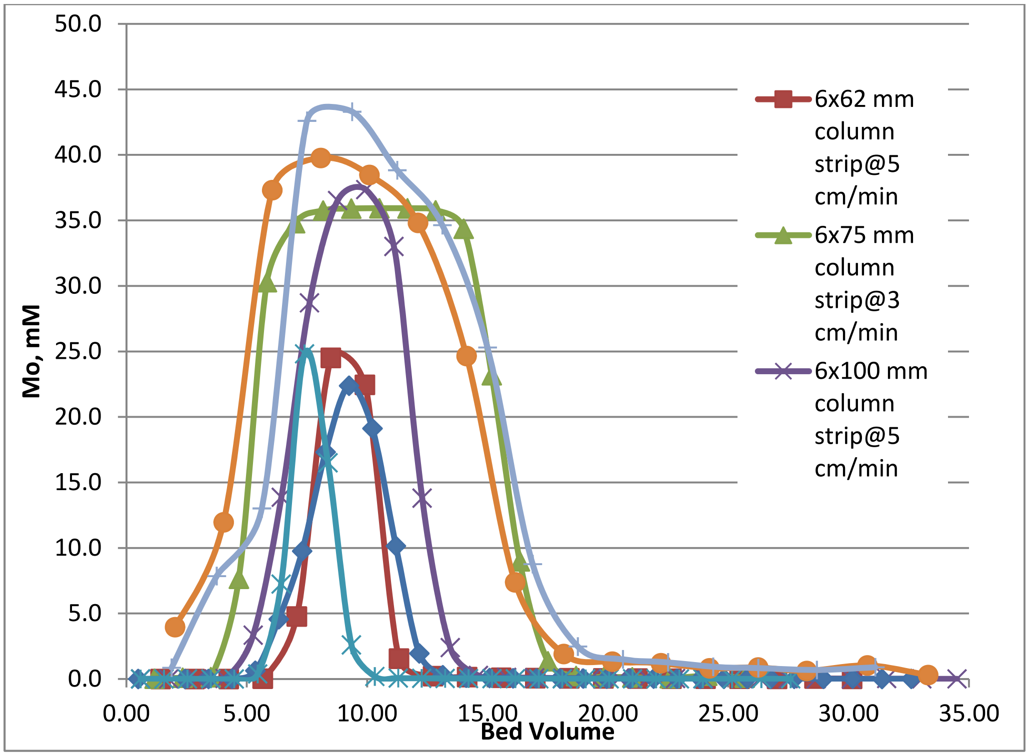

Figure 8. Counter-current stripping of Mo from titania columns with 0.1 M NaOH.

Experimental

Titania sorbent (TiO_2, 80 µm, 60 Å) was purchased ZirChrom Separations, Inc. (Anoka, MN). Alumina, (Al_2O_3, 75-150 µM, 60 Å) was obtained from Sorbent Technologies.

Uranyl nitrate, $UO_2(NO_3)_2$, solutions were prepared by dissolving a known amount of uranium metal in 8 M HNO_3. The resulting solution was titrated in presence of oxalate and H^+ was adjusted with concentrated HNO_3. Molybdenum was added as 0.3 M Na_2MoO_4, pH 0 solution. ^{99}Mo was obtained from a commercial ^{99m}Tc generator by stripping with 1 M NH_4OH, evaporating to dryness and dissolving in nitric acid.

Isotherm data were obtained by equilibrating 10 ± 1 mg of sorbent with 1 mL of 450g-U/L containing appropriate amount of Mo for 24 h at 60 °C.

The amount of activity in the aqueous samples was determined using a NaI(Tl), HPGe well detector or NaI(Tl) flow-through detector. ^{99}Mo was quantified by measurement of its 739 keV γ-ray. The activity of ^{99}Mo in each sample was corrected for decay.

The Omnifit chromatography columns (VWR Internal, West Chester, PA) were packed with titania sorbent and tested in the experiments. An AKTA Purifier unit (GE Healthcare, Piscataway, NJ) was used in the frontal and lab-scale Mo recovery experiments. During frontal and lab-scale Mo recovery experiments, the temperature of the column and the mobile phases was controlled by heat tapes, heating coils, and solution heating.

Future Experiments

Experiments will be performed to verify the behavior of other fission products in the Mo-recovery step. A 4 g depleted uranium (DU) target encapsulated in aluminum casing will be irradiated at the 20 MeV Argonne Linear Particle Accelerator (LINAC). Irradiation will be done using a tungsten photoconverter to generate high energy x-ray that will generate photofissions in the target. The target will be irradiated for 6 hours at 18 MeV and 200 microA; the expected ^{99}Mo yield, after 14 h cooling time is 0.6 mCi.

The target will then be disassembled and the DU foil will be dissolved in concentrated nitric acid. The irradiated DU solution (~ 10 mL) will then be added to a 500 mL of 450 g/L uranyl nitrate solution, 7 mM Mo, 1 M HNO_3 to produce a solution representative of the production-scale dissolved, irradiated LEU target solution. The solution will be passed through a 2x10 cm TiO_2 column at 5 cm/min. The expected loading time is ~ 30 min. 0.1 M NaOH solution was chosen to strip Mo from the column in order to best reflect current chemical conditions during process target digestion or to best align with subsequent Mo purification steps. Therefore 470 mL is expected to recover 95±5% of Mo in 30 min. The eluent (waste) is expected to contain all of the actinides, lanthanides, alkali and alkaline earth metal ions. The Mo-product stream is expected to contain a fraction of the fission products known to have chemistries somewhat similar to Mo, specifically elements known to be present as oxoions or anions in acidic solution. Therefore, the Mo product stream is expected to contain a small fraction of As, Se, Nb, Tc, Ru, Rh, Sn, Sb, Te as well as the iodine not volatilized in the dissolution; the fraction in the Mo product is assumed to be 1%. The K_d values for these anions in 0.1 M HNO_3 tend to be quite a bit lower than that of Mo; therefore, it is likely that a significant fraction of As, Se, Nb, Tc, Ru, Rh, Sn, Sb, Te, Br, and the remaining I will be found in effluent and wash waste streams and not in the Mo product stream.

It is anticipated that these experiments will be performed in late October or early November.

Conclusions

NCP-MTZ design method along with VERSE simulations was utilized to determine intraparticle diffusivity, MTZ and column designs. The results of scale-down indicate that Mo can be fully loaded on the proposed titania columns and then recovered by counter-current stripping with 0.1 M NaOH. By using the largest diameter column and intermediate flow rates, the Mo recovery operation should be completed in less than one hour. in 450 gU/L $UO_2(NO_3)_2$ and 1 M HNO_3

4. Elecrochemical Dissolution of LEU Foils in Bicarbonate Solution

Under normal conditions, uranium metal is only slowly digested in NaOH. With an aid of H_2O_2, the digestion can be accelerated, but the digestion is cumbersome and difficult to control [9].

High-temperatures are needed to accelerate the digestion with sodium hydroxide, which necessitate the use of a high pressure vessel to reach temperature of ~275º C [10]. A low-temperature, low-pressure procedure employing anodic oxidation of the uranium metal into basic bicarbonate media is under development, with consequent precipitation of uranium, alkaline-insoluble fission and activation products, and carbonate from the solution by the addition of calcium oxide, followed by the sorption of Mo-99 on an anion exchanger (e.g., BioRad AGMP-1)--Figure 9. The aim of this study was to verify the feasibility of this method and to identify key optimizing factors for the development of an industrial-scale procedure.

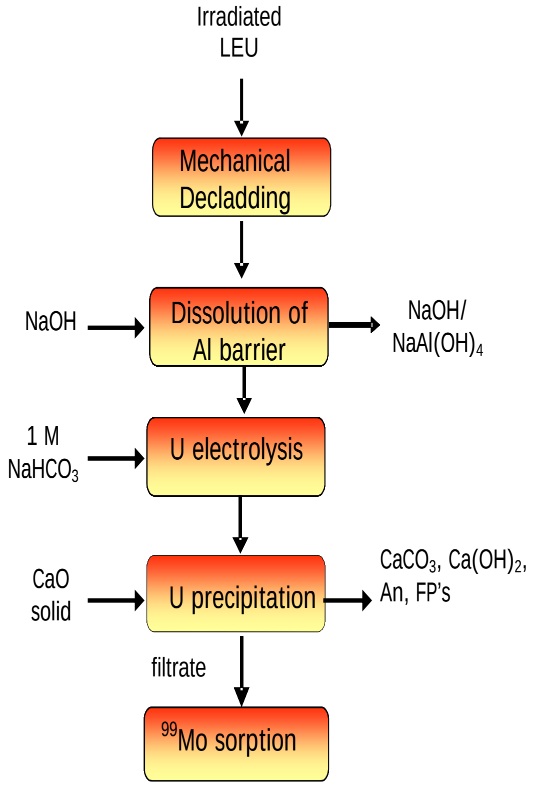

Figure 9. Block-diagram of a frontend process for ^{99}Mo production using LEU-foil electro-dissolution.

Electrolysis Experiments

The oxidation of uranium metal is assumed to proceed quickly through U(III), producing U(IV) oxide. Then, according to literature data, the oxidation of UO_2 proceeds through the formation of UO_{2+x} species on the surface until $UO_3 \cdot 2H_2O$ is formed [11]. Hexavalent uranium has rather high solubility in the presence of carbonate/bicarbonate ions [12]. The dissolution occurs when these negative ions reach the positively charged surface of the uranium anode.

Our preliminary tests showed that 20-22 g DU foils are completely dissolved within 1.5 hours. The foils were connected to anode lead via a clip, hanging freely in the solution, while the solution was intensively stirred. However, just hanging the irradiated foils during the dissolution may not practical as there is chance of dropping the foil in the dissolution vessel. Therefore, an anode basket or a cage should be utilized.

The following dissolution tests were conducted using a high current DC power supply by Magna Power with a voltage range of 0- 32 V and a current range of 0-64 Amps. The current was kept constant at 20 A in these tests. A two-step dissolver required for this process has been fabricated. Previously [13], the digester consisted of two chambers. However, to minimize the physical dimensions of the apparatus, we have changed it to a one-chamber dissolver with a stirring rod coming through the bottom (Figure 10). After removing the uranium foils from the targets, the uranium foils (bound by a 40-µm Al fission-recoil barrier) are placed in the dissolver to dissolve the Al barrier using a sodium hydroxide solution. After dissolution of the Al, the $Al(OH)_3$-containing solution is drained through a tube with a ball valve. The tube is located at the bottom of the dissolver (Figure 11). After a rinse, a sodium-bicarbonate solution is added in the dissolver, and the uranium foil electrolysis begins.

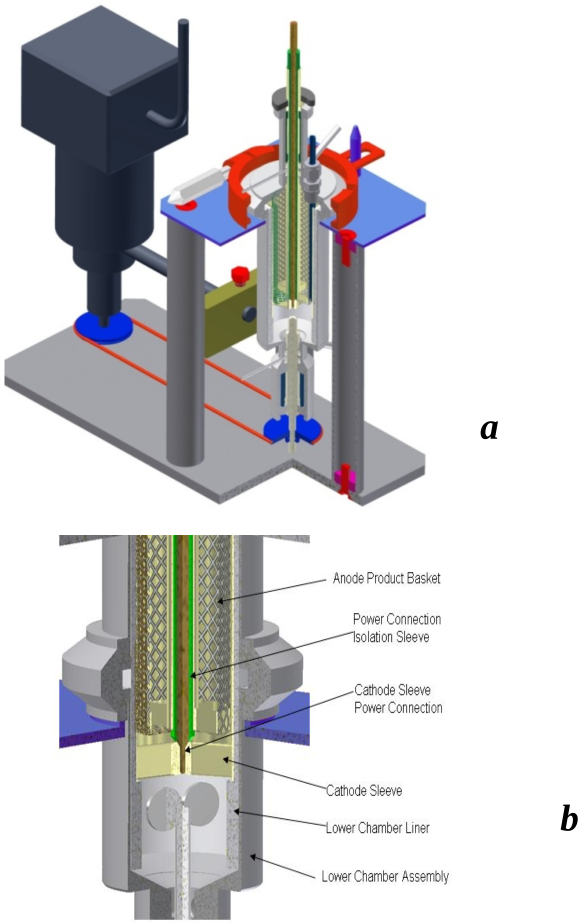

Figure 10 (*a* and *b*). Sketches of electrochemical dissolver with a motor and *(b)* Ni anode basket and cathode sleeve

There is a temporary shortage of full size 4"x4" DU foils at Argonne. Therefore, we have dissolved 2 DU foil strips of approx. 4"x1" (10.2cm x2.7 cm) dimensions and about 7.85 g each. The foils were placed in the anode basket and attached to it with two small washers tightened together with a bolt and a nut. We have found that the dissolution rate is very high at the beginning of the process—about a quarter of U is dissolved in first 15 min. However, the dissolution rate slows down after that. The situation is complicated by the fact that the dissolution is faster at the areas of the foil that are freely exposed to the solution. After about 90 minutes of the dissolution, the foils in both cases broke into 2 small pieces that accumulated at the bottom of the basket. It is unclear if the dissolution still occurs at this point since there might be no electrical contact between the foil pieces and the anode basket. The solution was stirred at around 1800 rpm, and the turbulent flow may have eliminated the contact between uranium metal and the anode. The amount of foil left was 0.67 g in the first test and 0.43 g in the second test. One of the pieces and the anode basket are shown in Figure 12. We are planning to re-design the anode, probably using a spring-loaded cage to contain the foil pieces until their complete dissolution.

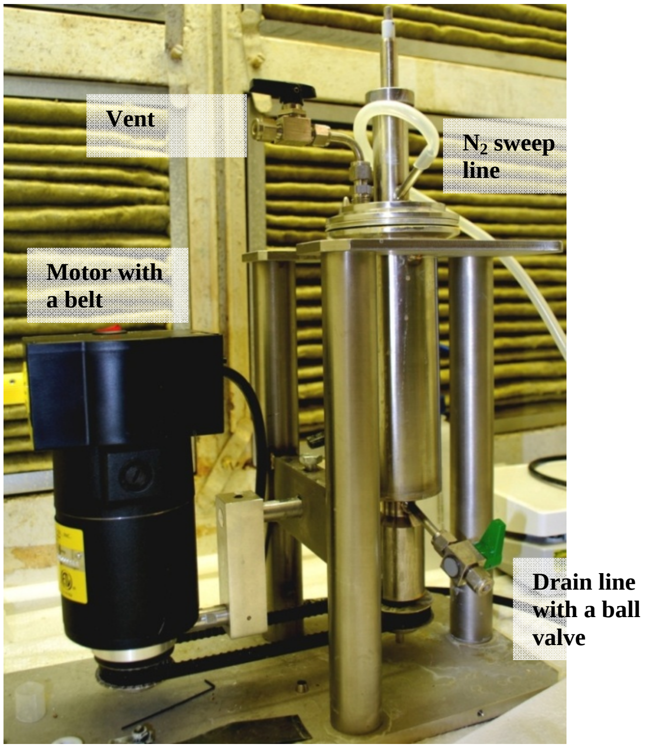

Figure 11. Electrochemical dissolver with a stirrer.

Figure 12. Anode basket and remaining U foil

Future work

We are planning to conduct a series of tests using depleted uranium foil as well as the low-burn-up irradiated DU foil. We will study molybdenum recovery and the behavior of other fission and activation products in all steps of the frontend process.

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