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Optimization of the Dissolution of Mo Disks

D.A. Rotsch, P. Tkac, G.F. Vandegrift

Nuclear Chemical Engineering Department
Nuclear Engineering Division
Argonne National Laboratory, 9700 S. Cass Ave., 60439 Argonne – United States

ABSTRACT

NorthStar Medical Technologies, LLC (NorthStar) plans to produce ^{99}Mo , via the $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ reaction, at the University of Missouri Research Reactor (MURR), as a short-term solution to meet demands. NorthStar's longer-term solution is to produce ^{99}Mo via the photonuclear reaction $^{100}\text{Mo}(\gamma,n)^{99}\text{Mo}$ from the irradiation, driven by the electron linear accelerator, of ^{100}Mo -enriched targets. Processing irradiated targets from either production route requires dissolution in hydrogen peroxide. Subsequent processing steps include partially evaporating the solution, removing impurities via precipitation, and converting the final solution to a 5 M hydroxide solution. Argonne National Laboratory has optimized this process by reducing processing time from more than 8 hours to less than 3 hours per 300 g batch of Mo. Recently, Argonne demonstrated the enhanced dissolution process on a larger scale (600 g batches) on disks of varying size. Modifications to the dissolution equipment are underway to adapt the process from benchtop to hot cell.

1. Introduction

Argonne National Laboratory (Argonne) is funded by the National Nuclear Security Administration's Office of Material Management and Minimization to assist NorthStar in developing the technology needed to bring both its $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ and $^{100}\text{Mo}(\gamma,n)^{99}\text{Mo}$ technologies to fruition. As part of Argonne's development activities, significant work has been performed to optimize disk processing [1-5]. As shown in earlier Argonne work, the method used to fabricate the target is crucially important to the dissolution rates of the target. Argonne is working closely with Oak Ridge National Laboratory (ORNL) to optimize target fabrication techniques in terms of both ease and efficiency of fabrication and rate and effectiveness of irradiated target-disk processing. ORNL experts are developing the means to optimize target-disk fabrication, and Argonne is developing the means to process molybdenum using materials fabricated at ORNL [6,7].

NorthStar's current baseline uses pressed and sintered Mo-metal disks as targets. Previous studies have found that high sintering temperatures, in general, lead to higher theoretical disk density, thus increasing production yields, but also lead to decreased dissolution rates. The porosity of the disk is very important for fast dissolution kinetics. However, in a few cases, disks with high packing density and low open porosity dissolved quickly (0.6 g/min), which could be related to the Mo particle size.

NorthStar will soon produce ^{99}Mo using the $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ production route at the University of Missouri Research Reactor (MURR). According to NorthStar, processing 300 g batches takes ~5-6 hours to complete. The processing time depends on the total mass of Mo. Argonne previously demonstrated that processing 300 g of target material can be accomplished in less than 3 hours [1]. Herein we report our attempts to optimize the dissolution of 600 g batches.

2. Experimental

Sintered Mo disks provided by NorthStar from a commercial supplier and from ORNL from their fabrication activities were dissolved at Argonne. Up to 600 g of Mo disks was dissolved in 50% hydrogen peroxide in a glass reaction vessel. The hydrogen peroxide used was 50 wt% peroxide stabilized by Sn (Aqua Solutions, Inc., technical grade, #H30504L, or Sigma-Aldrich #516813). As the natural-Mo disks were dissolved in the peroxide, the solution was repeatedly drained into an evaporation/concentration vessel and fresh hydrogen peroxide was added in the dissolution vessel. In this manner, the dissolution and evaporation steps were performed in parallel with partial solutions. Gentle heat (50 °C) was applied under vacuum to the initial volumes received in the evaporation/concentration vessel to destroy excess hydrogen peroxide and to begin the evaporation process (excessive heating caused rapid expulsion of gases and froth formation upon subsequent additions of dissolved Mo disks). As a safety precaution, a relief valve was attached to the evaporation vessel, to relieve the vacuum pressure and further minimize overflow risks.

During dissolution, copious amounts of vapor were evolved and were trapped in a 3 L round bottom flask equipped with three high-capacity condensers. A Julabo FL 1701 with cooling capacities: 1.7kW at 20°C, 1.1kW at 0°C, 0.85kW at -10°C, and 0.4kW at -20°C and flow rate capacity of 23 L/min was used. as a source for cold water for the condensers.

After complete dissolution, the final portion of dissolved Mo was transferred to the evaporation vessel. To assure a high yield of molybdenum, the dissolution vessel was rinsed with KOH (900 g of 85% KOH in 740 mL of H₂O) in portions and then transferred to the evaporation vessel. The next step after evaporation was to finish destroying the hydrogen peroxide and to bring the solution to the desired composition. Because the reaction of KOH with H₂O₂ is vigorous, this step was completed with extreme care. The combined solutions were heated to destroy peroxide and to bring the solution to the desired volume if needed. The evaporation vessel was drained into a large plastic bottle and the solution was filtered through a high-capacity filter—Polycap 36 TC (0.6/45 μm). The filtration step was performed under a vacuum and usually took ~15 minutes. After filtration, KOH was added to make ~0.2 g-Mo/mL as K₂MoO₄ in 5M KOH solution.

3. Results and Discussion

Processing of sintered Mo disks

The dissolution and evaporation setup is shown in Figure 1. Table 1 summarizes the optimization work performed at Argonne thus far [1,3,4]. In short, 75–300 g batches of Mo disks were dissolved, and the hydrogen peroxide concentration, the equipment, and the glassware used were adapted and modified to decrease processing times and increase processing efficiencies. Most notably, the total processing time decreased from using 30% to 50% H_2O_2 . The processing time decreased by 75% with this minor change and was attributed to the minimal time required for evaporation of excess liquid. Using a higher concentration of H_2O_2 meant that less H_2O_2 solution was needed to completely dissolve the Mo disks, and thus less liquid needed to be removed during evaporation.

The equipment

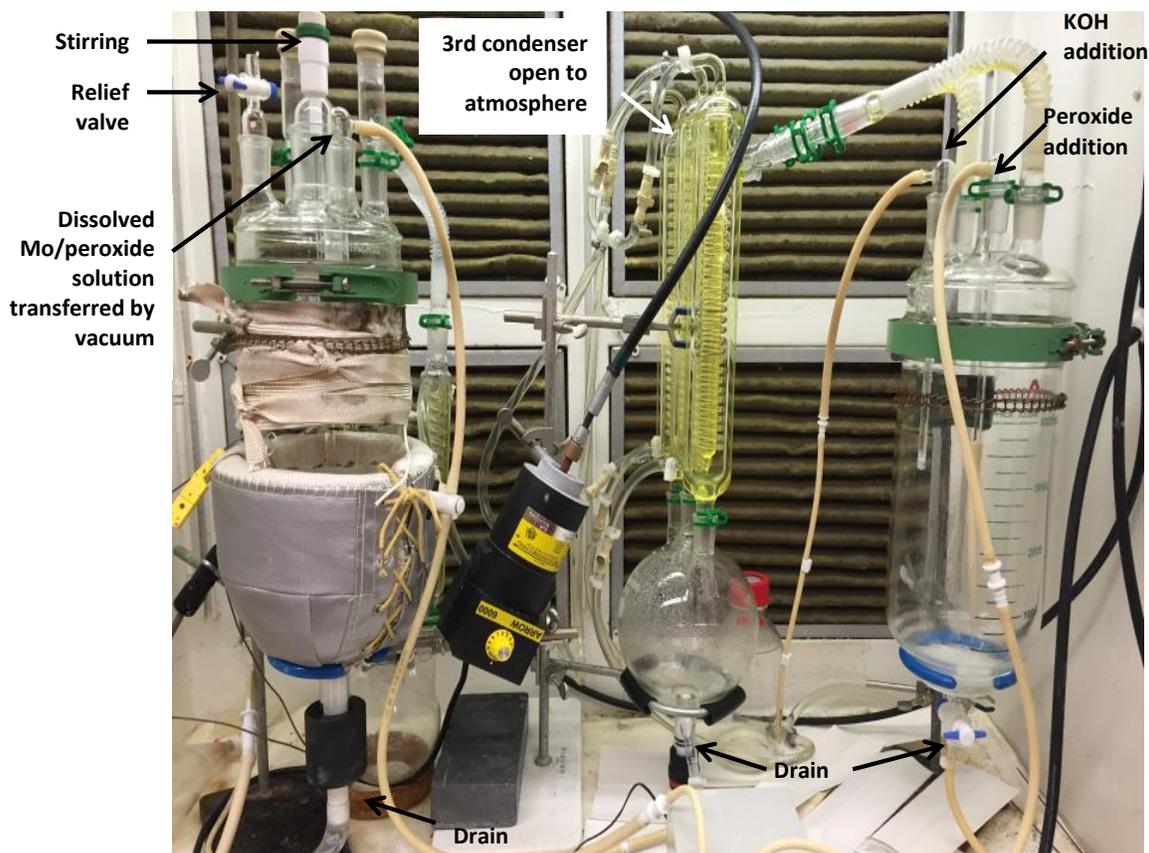


Figure 1. Modified dissolution, exhaust condensation, and evaporation setup. Evaporation vessel (left), is heated with an over-sized heating mantel and heat tape. The associated condensation vessel is visible behind the evaporation vessel. The dissolution vessel (right), is connected to the evaporation vessel through the lower drain. The associated condensation vessel, (middle) is connected by two flexible adapters to the dissolution vessel and can be drained at any point during the experiment through a lower drain.

In the present studies, 600 g of Mo disks were dissolved in 50% H₂O₂ in an upgraded system from our previous efforts [1]. These upgrades included using three high-capacity condensers, a 3 L collection flask equipped with a bottom drain spout, and a Julabo F26 ED (0.26-kW cooling capacity at 20°C and flow rate of 15 L/min) chiller. The condensers were used to replace the lower efficiency condensers, to trap the majority of the vapors evolved during the dissolution process. A treacherous flow path vented to atmosphere was established (Figure 1, right side). Here the evolved gases flow up and out of the dissolution vessel to the high-efficiency condensers in two parallel flow paths, then down the water cooled jackets and up a single high-efficiency condenser before the gas phase is exhausted to the atmosphere. The parallel flow paths were established to decrease the internal pressure by increasing the volume capacity of the flow path. A 3-L round bottom was put in place to collect the condensation of the evolved dissolution vapors. The lower drain spout allows for easy removal of the volume collected. During the increased mass dissolution experiments, this vessel needed to be drained at least once during processing. The new chiller proved to be more efficient than the previous one but was also unable to keep up with the exothermic process of the dissolution of Mo metal. On several occasions, the dissolution needed to be halted by ceasing the addition of H₂O₂ in order for the chiller to reestablish an acceptable chilled water supply.

No significant changes were made to the evaporation vessel during development. The heating mantel, heat tape, and condensers performed as expected. Gently heating the solution that is transferred from the dissolution vessel accelerates the decomposition of hydrogen peroxide. The solution, in general, was not heated to evaporation temperatures until after the complete dissolution of Mo and the transfer of that solution into the dissolution vessel. If evaporation was required, the vessel was heated with both the heat tape and the heating mantel. Vacuum was applied at all times on the evaporation vessel.

Dissolution of 600 g of 26x1 mm disks

The dissolution of 600 g of 26x1 mm sintered disks was not significantly different from the dissolution of 300 g batch [1]. Dissolution rates were approximately the same from the optimized 300 g dissolution rates. With twice the mass of disks, approximately twice the amount of H₂O₂ was required to fully dissolve 600 g of disks and required about twice the amount of time. The slight increase in H₂O₂ can be attributed to the self-destruction of H₂O₂. Hydrogen peroxide decomposes with heat, and this reaction is vigorous and exothermic; therefore, self-destruction was expected.

Dissolution of 29.5x0.5 mm disks

The dissolution rate of these larger diameter and thinner disks was significantly faster than the 26x1 mm disks and required considerably less H₂O₂, ~3 L less (Table 1). The faster dissolution rate can be attributed to the larger surface area of the disks. Assuming that the porosities of the disks are equal, the surface area of the 29.5x0.5 mm disks is 1413.24 mm² while the surface area of the 26x1 mm disks is 1143.54 mm². The increased surface area allows for greater contact with the H₂O₂ and thus more surface in which the reaction may occur. Furthermore, as the disks dissolve, layers of Mo are stripped away. The thinner disks have fewer layers than the thicker disks. The reaction itself was not noticeably more vigorous than that of the 26x1 mm disks. The

H₂O₂ economy of this reaction was better and thus did not require any evaporation, driving down the total processing time.

Table 1. Results from experiments to optimize large-scale dissolution

Disks (mm)	Mo (g)	H ₂ O ₂ (%)	H ₂ O ₂ (L)	Dissolution (hours)	evaporation (hours)	total (hours)	total dissolution rate
26x1	75	50	0.75	0.5	1.5	2	0.63g/min
26x1	75	50	0.7	0.5	1.2	1.7	0.74g/min
26x1	75	30	0.9	0.5	3.5	4	0.31g/min
26x1	300	50	2.9	2.5	5.8	8.3	0.6g/min
26x1	300	50	3.1	2.7	2	5.0	1g/min
26x1	300	50	4.5	2	7	9.2	0.55g/min
26x1	300	30	6.3	1.5	6.4	8.2	0.61g/min
26x1	300	50	4.5	1.5	0.6	2.3	2.2g/min
26x1	300	50	4.5	1.3	0.7	2.2	2.3g/min
26x1	603.7	50	9.5	2.5	1.5	4.5	2.24g/min
26x1	600.5	50	9.0	2.75	1	4.0	2.5g/min
26x1	602.4	50	6.5	2.0	1.5	3.75	2.68g/min
29.5x0.5	596.8	50	6.8	1.8	0	2.25	4.42g/min

Adapting optimized dissolution system from the benchtop to hot cell operations

Processing production level quantities—thousands of curies (Cis)—of irradiated molybdenum will be performed in a hot cell. NorthStar is currently designing their hot cell for this work. One of the primary concerns is that the system described in section 1 of this report is comprised entirely of glass. Glass could break within a hot cell, where metallic manipulators perform the operations needed for processing hundreds of grams of irradiated Mo. Furthermore, the system

requires cleaning between processing runs, and periodic maintenance. Therefore, there is a need to demonstrate that the equipment can be set up, maintained, and operated in a hot cell environment. Argonne has configured a hot cell mockup to determine the required dimensions for the optimized system and ensure operations can be performed within the confined space of a hot cell.

Figure 2 shows an image of the hot cell mockup. The system fits within the dimensions of 139.7 cm x 111.76 cm x 160.02 cm (w x d x h). This layout allows for 71.12 cm of working space in front of the setup. These dimensions allow ample room for an antechamber tray pass through, additional valves, and other required attachments (i.e., condenser water lines, liquid disposal lines, etc.). There is also room for retrieving disks from irradiation holders, preparing disks to add to the dissolution vessel, performing standard operations, and storing the manipulators when not in use. The manipulators must be able to reach from floor to the height of the tallest vessel (0–127 cm). The system components are modular so that individual components can be removed and replaced when maintenance or replacement is needed.

Because they are too heavy and cumbersome to remove with manipulators alone, the modules are equipped with rings on the top, to allow hooks from cranes to lift them. The manifolds are made of lightweight aluminum and can be bolted to the floor to avoid inadvertently knocking them over. Alternatively, the bases could be made to fit into notches in the hot cell floor or a lock and key mechanism could be devised. A large exterior hot cell door would be required to bring the modules in and out of the hot cell, or a long antechamber in which the modules could lay on their sides.

Flexible adapters are used to connect the evaporation vessel to its condenser system and dissolution vessel to its condenser system. These flexible adapters are required, unless fixed positioning is used for the system components. Even then, the system may prove difficult to wield with manipulators. Every connection must be gas tight, to provide adequate vacuum and no loss of material or vapor. It is unclear at this point if flexible or rigid connections better suit the system.



Figure 2. Hot cell mockup with view from operator standpoint. No leaded glass is in place. From left to right: evaporation vessel, evaporation vessel condenser and collection vessel, dissolution vessel condensers and collection vessel, and dissolution vessel.

Evaporation System

The evaporation vessel (Figure 3A and 3B) is currently 127 cm in height, with a diameter of 34.29 cm at its widest point. The associated collection system (Figure 3C) has a height of 96.52 cm and a diameter of 24.13 cm at its widest point. A glass evaporation vessel is needed to view the interior liquid level, as the vessel is too cumbersome to weigh. Graduations can be marked on the exterior of the vessel to indicate the solution volume. The vessel alone is ~85 cm tall. The vessel's head, shown in Figure 3B, adds another 34.29 cm from the combined 17.78 cm head and the 16.51 cm adapter to the stirring mechanism. The condenser system is attached with flexible adapters with glass 24/40 (standard taper) adapters.

The condenser system connects to the evaporation vessel by two pathways, to maximize the flow path volume. Two high-efficiency condensers and a gas inlet are affixed to a 3 L round bottom vessel with a bottom drain. The bottom drain is currently controlled with a twist stop cock that can be replaced with a t-valve (for use with manipulators) or with a remotely-operable valve. Condensate must be drained after every process.

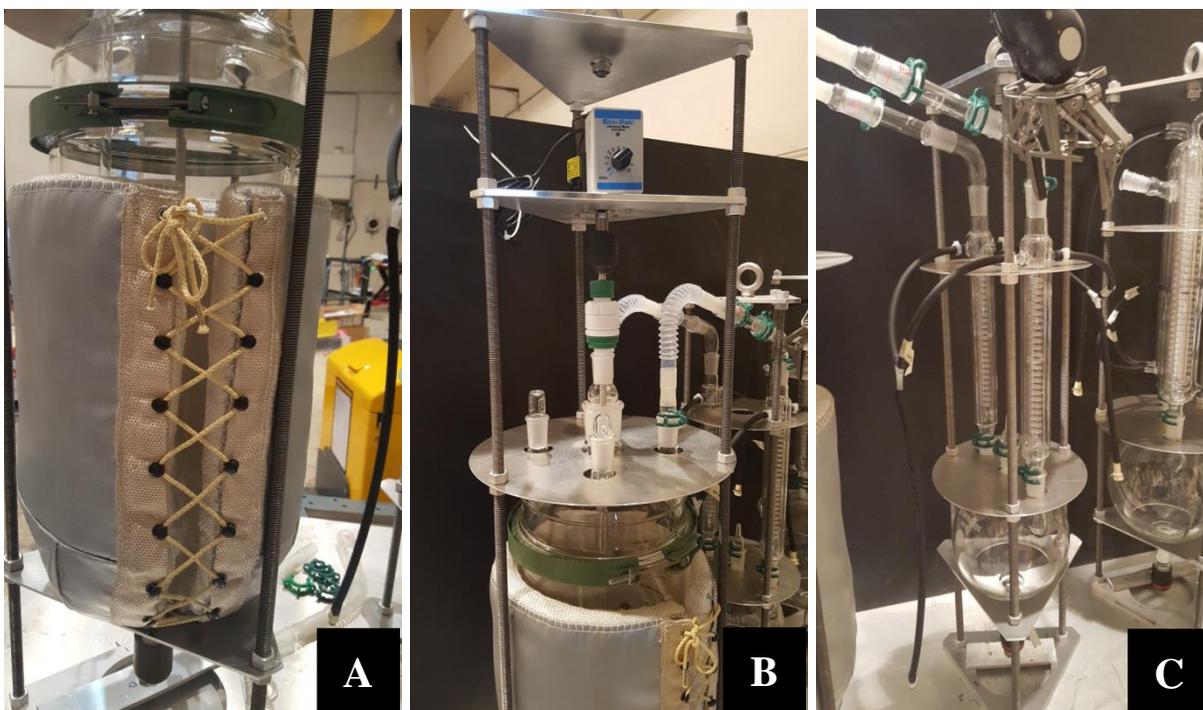


Figure 3. Evaporation vessel with heating mantle on 10 L reaction vessel (A); evaporation vessel head with associated stirrer and connections to condenser system (B); and evaporation condenser system (C).

Dissolution System

The dissolution vessel (Figure 4, A and B) has a height of 96.52 cm and a diameter of 30.48 cm at its widest point. Figure 4C shows the associated condenser system; it has a height of 101.6 cm and a diameter of 27.94 cm at its widest point. The glass vessel is needed to view the dissolution process. The operator must be able to observe the disks, the color of the solution, and the height of the reaction foam. The vessel itself is ~66 cm tall. The vessel's head is ~16.5 cm tall and the flexible adapters add another 5.08 cm. The condenser system is attached with flexible adapters with glass 24/40 (standard taper) adapters.

The condenser system connects to the dissolution vessel by two pathways, to maximize the flow path volume. Three high-efficiency condensers are affixed to a 5 L round bottom vessel with a bottom drain. The bottom drain is currently controlled with a twist stop cock that can be replaced with a t-valve (for use with manipulators) or with a remotely-operable valve. Condensate must be drained after every process. The central condenser is open to the atmosphere to avoid pressurization of the system.

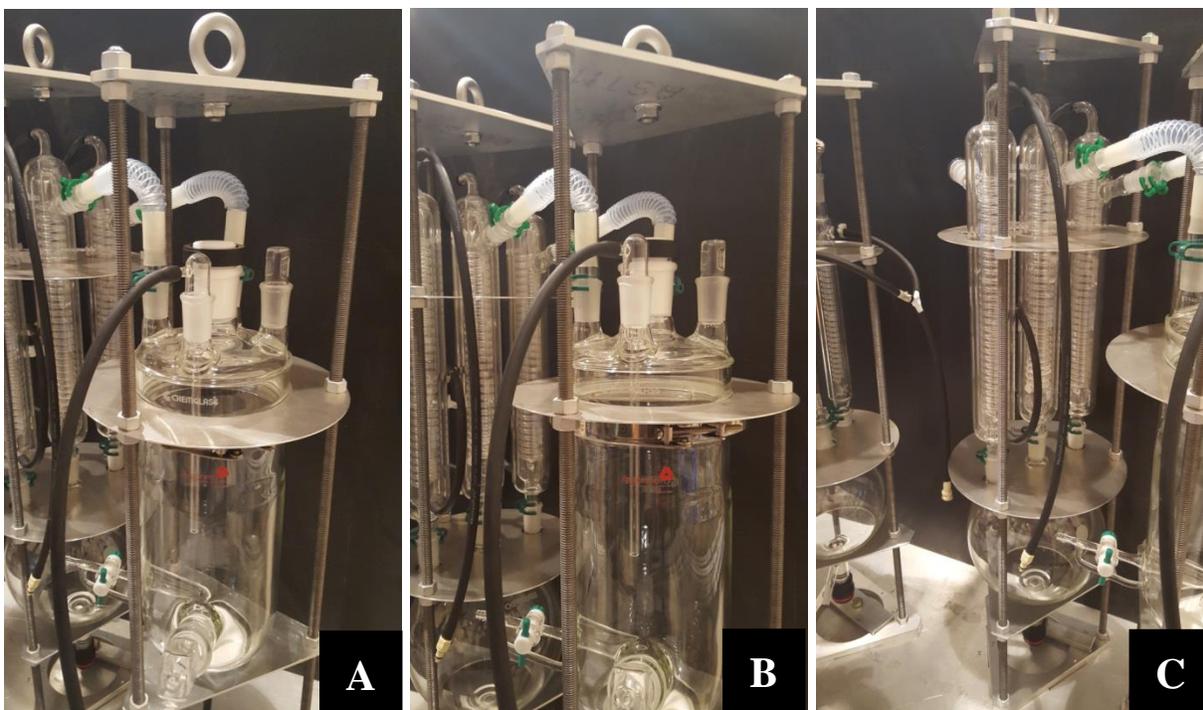


Figure 4. Dissolution vessel (A and B) and dissolution vessel condenser system (C).

Conversion to Stainless Steel

Stainless steel provides a chemically resistant material with durability that far exceeds glass. As previously mentioned, the dissolution and evaporation vessels must remain glass. A shield or shroud can be used to protect the vessels from inadvertent bumps with manipulators or other tools within the hot cell. Components eligible for conversion to stainless steel are the condensation systems (dissolution and evaporation), including the evaporation and dissolution vessel heads/lids. The vessel heads can be replaced with stainless steel flat caps to eliminate some of the headspace needed. Introducing the disks to process through the flat cap of the dissolution vessel can be accomplished by several methods. One is to include a slide mechanism, where the disks are loaded one at a time. Another, more efficient, method is to load the disks using an insert that is loaded with the disk (presumably the irradiation target holder), introduced into the dissolution vessel through a pass-through in the stainless steel cap, and a mechanism is used to release the disks into the vessel. The pass-through can be sealed with a plug once the target holder releases its payload. This requires a modest redesign of the dissolution holder. Flexible or rigid connections can be used to connect the modular systems together. Aside from the durability, an added benefit to condensation systems of stainless steel is that remotely-operated or electric valves can be used to drain the system, minimizing remote operator manipulations.

4. Conclusions

Dissolution studies were performed on 600 g of Mo disks with the optimized system, developed from multiple 300 g dissolution studies. As expected, the dissolution rates remained the same for 600 g 26x1 mm disks as for the 300 g 26x1 mm disks. The volume of H₂O₂ needed approximately doubled, as did the dissolution time. Dissolution of higher surface area disks proved to be more efficient in all aspects of processing. Processing 29.5x0.5 mm disks used less H₂O₂, took less time for dissolution, and needed no evaporation. Using the optimized system, the dissolution rates were on average 2.31 g/min and 4.44 g/min for 26x1mm and 29.5x0.5 mm disks, respectively. The increased condenser capacity helped minimize the amount of vapor to escape the system, conservatively estimated to be <5% escape. To eliminate all vapor escape requires a higher-capacity recirculating chiller.

A hot-cell disk-processing mockup has been demonstrated. This system used glass, but future plans are to design a stainless steel system.

5. Acknowledgment

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6. References

- [1] P.Tkac, D.A. Rotsch, D Stepinski, V. Makarashvili, G.F. Vandegrift, J. Harvey, "Optimization of the Processing of Mo Disks" Argonne National Laboratory, Report ANL/NE-15/46, January 2016.
- [2] P.Tkac, G. Vandegrift, and J. Harvey, "Dissolution of Sintered Mo Disks," Argonne National Laboratory, Report ANL/CSE-13/19, July 2012.
- [3] P. Tkac, G. Vandegrift, S.D. Nunn, and J. Harvey, "Processing of Sintered Mo disks Using Hydrogen Peroxide," Argonne National Laboratory, Report ANL/CSE-13/44 (September 2013).
- [4] P. Tkac and G.F. Vandegrift, "Dissolution of Sintered Mo Disks," Argonne National Laboratory, Report ANL/CSE-14/26, September 2014.
- [5] P.Tkac, K.E. Wardle, M.A. Brown, A. Momen, D.A. Rotsch, J.M. Copple, S.D. Chemerisov, R. Gromov, G.F. Vandegrift, "Chemical Processing for Non-uranium Production of ⁹⁹Mo/^{99m}Tc," Mo-99 Topical Meeting on Molybdenum-99 Technological Development, St. Louis, Missouri, September 2016.

[6] R.A. Lowden, R.R. Lowden, C. Bryan, "Powder Metallurgy Fabrication of Molybdenum Target Materials and Assemblies," Mo-99 Topical Meeting on Molybdenum-99 Technological Development, Boston, Massachusetts, September 2015.

[7] R.A. Lowden, S.D. Nunn, J.O. Kiggans Jr., R.J. Parten, Bryan C.D. "Powder Metallurgy Fabrication of Molybdenum Accelerator Target Disks", Oak Ridge National Laboratory, Report ORNL/TM-2014/238, July 2015.