ANL Activities in Support of Accelerator Production of $^{99}$Mo through the $\gamma$/n reaction on $^{100}$Mo

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ABSTRACT

Argonne National Laboratory is supporting development of accelerator-based production of $^{99}$Mo using photonuclear reaction $^{100}$Mo$(\gamma, n)^{99}$Mo with an enriched $^{100}$Mo target. Argonne is involved in Mo target irradiation using a linac with the ability to cool a Mo target with power deposition up to ~1 kW per gram. Studies on target processing concentrate on the development of optimum disk properties that would allow fast dissolution rates and high theoretical density. After dissolving enriched $^{100}$Mo disks in hydrogen peroxide, the solution is converted to potassium molybdate (0.2g-Mo/mL) in 5M KOH and loaded into the TechneGen generator. After the $^{99}$Mo is depleted, the solution containing ~1.8kg of potassium per kg of Mo needs to be treated to recover the valuable $^{100}$Mo for future production of sintered Mo disks. Recovery of Mo requires high purification factors from potassium ($\sim 10^5$) and high recovery yield of Mo. Experimental data on Mo disks dissolution and recovery of Mo will be presented.

1. Introduction

The National Nuclear Security Administration’s (NNSA’s) Global Threat Reduction Initiative (GTRI), in partnership with commercial entities and the US national laboratories support development of technology for conversion of civilian facilities using high enriched uranium (HEU) to low enriched uranium (LEU) fuels and targets. GTRI is also establishing a reliable U.S. domestic supply, and assisting potential producers to provide medical isotope $^{99}$Mo without the use of HEU. Here we discuss the activities performed at Argonne National Laboratory (ANL) in collaboration with Los Alamos National Laboratory (LANL), Oak Ridge National Laboratory (ORNL), and NorthStar Medical Radioisotopes that support
The accelerator technology pathway for the production of $^{99}$Mo using photonuclear reaction $^{100}$Mo($\gamma$, n)$^{99}$Mo in an enriched $^{100}$Mo target. $^{99}$Mo can be produced by a high-power electron accelerator creating high energy photons directly in the Mo target ($^{100}$Mo enriched sintered disks) through bremsstrahlung process. A plot of the photonuclear cross section for this reaction is shown in Figure 1. The threshold for the reaction is 9 MeV. The maximum cross section is 150 mb at 14.5 MeV. A closed loop helium cooling system has been designed by LANL and ANL and is capable of dissipating up to 1 kW power per 12x1 mm sintered Mo disk (~1g of Mo).

![Figure 1. Photonuclear cross section of $^{100}$Mo and average bremsstrahlung photon spectra produced with a 20- and 35-MeV electron beam in a molybdenum target.](image)

After producing the required activity of $^{99}$Mo, the target is dissolved in hydrogen peroxide and converted to K$_2$MoO$_4$ in 5M KOH by adding concentrated solution of KOH. Final concentration of the solution is 0.2g-Mo/mL. Dissolution studies of Mo sintered disks were performed in order to better understand how the disks’ physical properties can affect the dissolution rates. From the production point of view, it is desirable to have the highest density target; putting more $^{100}$Mo in the accelerator beam would lead to the $^{99}$Mo yield being higher. However, due to a short half-life of $^{99}$Mo, it is also necessary that the processing time for the irradiated target disks be as short as possible. Approximately 1% of $^{99}$Mo is lost every hour due to its decay. After dissolution, the solution of K$_2$MoO$_4$ in 5M KOH is loaded into the TechneGen generator to separate Tc from Mo. After the $^{99}$Mo in the feed solution is depleted by decay, the solution needs to be treated to recover valuable $^{100}$Mo for future production of sintered Mo disks. However, during the production of $^{99}$Mo by ($\gamma$, n) reaction on $^{100}$Mo target, several byproducts are formed. Therefore, recycle of Mo will require conversion of K$_2$MoO$_4$ in 5M KOH solution to MoO$_3$, and purification from other metals present in Mo solution. Focus is made on purification from Al, Fe, Zr, Nb, W, Rh and Sb. Most challenging is purification of molybdenum from potassium. The initial K/Mo mass ratio in a 5M KOH solution is ~1.8 or higher depending on type of TechneGen generator (1-20Ci of $^{99}$Mo). Purified material should contain <70ppm of potassium, preferably ~20ppm (purification factor ~10$^5$) and high Mo yield of >98%. After producing MoO$_3$ powder, Mo metal powder is made by reduction of the oxide with hydrogen under an inert atmosphere.
The general scheme for the molybdenum cycle from disk production through recycle of spent Mo solution is shown in Figure 2.

**Figure 2.** Diagram of molybdenum cycle from the disk production through the recycle

Experimental results presented here focus on disks processing and Mo recovery. There also is an active collaboration with ORNL regarding the disk production and recovery of Mo material. Recovered MoO$_3$ powder will be shipped to ORNL for reduction and production of new sintered Mo disks that will be tested for dissolution properties.

2. **Experimental**

2.1. **Sintered Mo disks**

All Mo sintered disks investigated in this work were supplied by NorthStar, and were prepared by pressing natural Mo metal powder and then sintered to make 12×1 mm disks. The disks properties that can significantly affect the dissolution kinetics and that were investigated are: (i) packing density; (ii) sintering history, and (iii) Mo-powder particle size. The packing density (%) was determined based on the dimension of the disk and compared to the density of Mo metal (10.22 g·cm$^{-3}$). The properties of the disks are described by a 3 digit code “ABC”. The first digit “A” refers to pre-sinter conditions of the metal powder before it is pressed. The second digit “B” is the pressing parameter and refers to the pressure that was applied during pressing. The third digit “C” refers to the final, post pressing sintering conditions. The actual conditions of sinter temperature and pressure are not known and are proprietary information of the disk manufacturer.
Dissolution studies were performed in a glass beaker using 40 mL of 30% hydrogen peroxide heated to 70°C. The reaction describing the dissolution of Mo metal in hydrogen peroxide is shown below:

$$2\text{Mo(s)} + 10\text{H}_2\text{O}_2 = [\text{Mo}_2\text{O}_3(\text{O}_2)\text{(H}_2\text{O})_2]^2^- + 2\text{H}_3\text{O}^+ + 5\text{H}_2\text{O} \quad \text{(eq. 1)}$$

The reaction is quite vigorous, and due to the auto-destruction of hydrogen peroxide to water and oxygen, produces a lot of bubbles:

$$2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2 \quad \text{(eq. 2)}$$

The auto-destruction of hydrogen peroxide is apparently catalyzed by the presence of the Mo disk. When auto-destruction of hydrogen peroxide is very vigorous, it competes with the oxidation of Mo (eq. 1), and much more hydrogen peroxide must be added to dissolve the disks.

During the dissolution, the solution turns yellow to orange depending on the concentrations of Mo and H$_2$O$_2$. After a complete dissolution of the disks, the solution of Mo in hydrogen peroxide is converted to highly alkaline solution by a careful addition of potassium hydroxide:

$$2[\text{Mo}_2\text{O}_3(\text{O}_2)\text{(H}_2\text{O})_2]^2^- + 8\text{KOH} = 4\text{K}_2\text{MoO}_4\cdot(\text{H}_2\text{O})_2 + 5\text{O}_2 \quad \text{(eq. 3)}$$

Addition of KOH to the Mo solution in hydrogen peroxide also produces a lot of bubbles and heat. The solution is further heated to destroy any residual peroxide, and additional KOH is added to yield a clear and colorless solution of potassium molybdate with 0.2 g-Mo/mL in 5M KOH. The solution of Mo in 5M KOH is ready to be loaded into the TechneGen (NorthStar) generator without any further purification.

### 2.2. Recovery of molybdenum

Precipitation of Mo was performed by adding glacial acetic acid, ethanol, or their mixture to solution of 0.2 g-Mo/mL in 5M KOH. The Mo precipitate was then repeatedly washed with concentrated acetic and nitric acid, re-dissolved in ammonium hydroxide and again precipitated and washed several times with acetic and nitric acid. After the final wash, the precipitate was re-dissolved and analyzed for potassium content using a potassium-ion-selective electrode and/or ICP-MS. The recovery of Mo was determined using a $^{99}$Mo spike or ICP-MS.

### 3. Results and discussion

#### 3.1 Dissolution of Mo sintered disks

##### 3.1.1 Sintering conditions

Different sintering conditions can significantly affect the packing density and dimensions of the disks. Aggressive pre-sinter conditions (“A”) lead to lower shrinkage, and lower theoretical densities of the disks. More aggressive sintering conditions (“C”) lead to greater shrinkage and a higher density of the disks, but usually slower dissolution rates. Figure 3 shows the packing densities for different A=0, 7, 9 and C=1, 2, 7, 9 parameters while
pressing parameter “B” was kept constant (B=4). Darker color of the data points in Figure 3 represents stronger sinter conditions (higher “C” parameter). In general, the packing densities increase with stronger sintering conditions, and the trend is more obvious for disks with lower “A” parameter. Data in Figure 3 show that stronger sinter “C” conditions lead to the lowest dissolution rates. In contrast, the best dissolving disks are with stronger pre-sinter (A=7-9) and weaker sinter conditions (C=1-2, light colored points). However, the packing densities for these disks were usually in the range of 86-88.5%. For the production of 99Mo, the disks with higher densities (90-92% or higher) are preferred to more efficiently utilize the beam and increase throughput. All disks with packing densities above 90% dissolved very slowly.

![Figure 3](image-url)

**Figure 3.** Effect of disks parameters A=0, 7, 9 and C=1, 2, 7, 9 on packing density and dissolution rates. The pressing parameter was constant; B=4. Darker color of the data points represents stronger sinter conditions (higher “C” parameter)

### 3.1.2 Different mesh size

The Mo powder was pre-sintered at three different conditions A=5, 7, 9, and then ground and sieved into different size ranges (Table 1). Then the disks were pressed at B=4 sintered at C=1, 2. The packing densities were in the range of 87.3-88.5%.

#### Table 1. Distribution of Mo particle sizes

<table>
<thead>
<tr>
<th>mesh</th>
<th>25</th>
<th>40</th>
<th>100</th>
<th>140</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>-500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size, µm</td>
<td>710-841</td>
<td>400-710</td>
<td>150-400</td>
<td>105-150</td>
<td>74-105</td>
<td>45-74</td>
<td>37-45</td>
<td>25-37</td>
<td>&lt;25</td>
</tr>
</tbody>
</table>

Originally, it was expected that the disks made of finer material would have a big impact on increasing the density, but only a small change in the density was observed for disks with weak sinter conditions (C=1, 2). The dissolution rate, however, increases dramatically with increasing mesh size (decreasing particle size) (Figure 4). The increase in dissolution rate for “542” and “942” disks made of -100 mesh and -500 meshes was more than a factor of two for the finer-particle disks. Also, several disks with A=7-9, B=4, and C=6-8 made from powder sieved through 20 mesh, and 400 mesh sieves were investigated. An increase in the packing densities with progressively increased sintering conditions is obvious for all pre-sinter conditions (Figure 5). The densities for -400 mesh disks are considerably higher than for -20 mesh disks with the same sintering conditions. This could indicate that stronger sintering conditions are important for increasing the packing density when using finer
particles, since the effect with C=1, 2 and -400 mesh powder was not very significant. Figure 5 also show the dissolution rates for disks made of Mo powder sieved through 20 and 400 mesh sieve and various “A” and “C” parameters, and B=4. As expected, the dissolution rates decrease as “C” increases. Experimental data confirm that size of the Mo powder used for a disk production can affect dissolution rate. In general, the disks made of finer particles (-400 mesh) can dissolve significantly faster than the disks made of -20 mesh powder.

**Figure 4.** Dissolution rates of disks with different sintered history made of powder with different particle sizes (for reference see Table 1). The data for disks made of >500 mesh are plotted as 600 mesh, although their actual size distribution was not determined

**Figure 5.** Comparison of packing densities and dissolution rates for disks pre-sintered and sintered under different conditions, and made from powder sieved through 20 and 400 mesh sieves
3.1.3 Different pressing conditions

From previous studies [1], we have learned that best dissolving disks are disks made from fine Mo powder (~400 mesh), pre-sintered at A=7-9 and sintered at lower conditions C=1-2; however, the densities for these disks are usually below 90% at standard pressing (B=4). Therefore, we investigated how different pressing conditions affect the packing density and dissolution rates. For this study, disks pre-sintered at A=7 and sintered at C=1, 2, 6 and 8 were investigated. The data for packing densities and dissolution rates are shown in Figure 6.

![Figure 6](image)

**Figure 6.** Dependence of packing densities and dissolution rates for disks pre-sintered at A=7, sintered at C=1, 2, 6, 8 on different pressing parameter (B=8-11)

The packing densities for the disks sintered at C=1 and 2 were in the range of 90.7-92.6% and 90.3-93.6%, respectively, but the dissolution rates (0.6g/min for C=1, and 0.4g/min for C=2) were not affected by increased pressing or densities. Observed dissolution rates for disks with densities above 92% are very good. Disks sintered at C=6 dissolved significantly slower and dissolution rates decreased with increased pressing (0.285-0.143g/min). Disks sintered at C=8 would not dissolve without additional heating (~100°C), and a negative slope for dissolution rates with an increase of the pressing parameter is obvious. Figure 7 shows optical micrographs images (provided by ORNL) of polished disks with A=7, B=9 and C=1, 2, 6, 8. Very slow dissolution of disks sintered at C=8 (Figure 6) can be explained by coalescence of particles and significant grain growth. The porosity of this disk is located within the grains, while the porosity of disks sintered at C=1, 2, 6 is located at the interfaces between the original powder particles (Figure 7). Figure 8 show the dependence of dissolution rates on sintering conditions for disks with densities ~92-94% pre-sintered at A=7. The images in Figure 7, and data in Figure 8 highlight the importance of optimum sinter conditions for fast dissolution of disks with densities >92%.
Figure 7. Optical micrographs of polished Mo disks pre-sintered at A=7, pressed at B=9 and sintered at C=1, 2, 6 and 8 (provided by ORNL). Much of the apparent porosity in the image of 791 disk is due to pull out of poorly bonded particles during the grinding and polishing operations.

Figure 8. Dissolution rates of disks pre-sintered at A=7 and sintered at different conditions with densities ~92-94%.
3.2 Mo recovery

Experiments were performed using 1-5mL of 0.2g-Mo/mL solution of K$_2$MoO$_4$ in ~5M KOH. Glacial acetic acid, ethanol, or their mixture was used to precipitate molybdenum from 5M KOH. Ethanol (EtOH) produces a white precipitate of potassium molybdate, while adding acetic acid (AcA) to alkaline solution of K$_2$MoO$_4$ produces more precipitate, which could indicate presence of molybdenum-acetate species. Usually about 95-99% of potassium is removed in first 4 steps that include (i) precipitation of Mo, (ii) washes with acetic and nitric acid, and (iii) dissolution in NH$_4$OH followed by precipitation with acetic acid. Table 2 shows the fractions of potassium removed and Mo losses for acetic and nitric acid washes.

<table>
<thead>
<tr>
<th>step</th>
<th>reagent</th>
<th>K removed</th>
<th>Mo loss</th>
<th>solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo ppt</td>
<td>AcA; EtOH/AcA</td>
<td>65-75%</td>
<td>0-3%</td>
<td>cloudy; clear</td>
</tr>
<tr>
<td>wash 1</td>
<td>AcA</td>
<td>10-15%</td>
<td>&lt;1%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 2</td>
<td>HNO$_3$</td>
<td>5-10%</td>
<td>0-15%</td>
<td>cloudy</td>
</tr>
<tr>
<td>diss. + ppt</td>
<td>H$_2$O+NH$_4$OH</td>
<td>0-5%</td>
<td>0-3%</td>
<td>cloudy</td>
</tr>
<tr>
<td>wash 3</td>
<td>HNO$_3$</td>
<td>&lt;0.5%</td>
<td>0-15%</td>
<td>cloudy</td>
</tr>
<tr>
<td>wash 4</td>
<td>HNO$_3$</td>
<td>&lt;0.1%</td>
<td>0-2%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 5</td>
<td>HNO$_3$</td>
<td>&lt;0.1%</td>
<td>&lt;0.5%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 6</td>
<td>HNO$_3$</td>
<td>&lt;0.1%</td>
<td>&lt;0.5%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 7</td>
<td>HNO$_3$</td>
<td>&lt;0.1%</td>
<td>&lt;0.5%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 8</td>
<td>HNO$_3$</td>
<td>&lt;0.1%</td>
<td>&lt;0.5%</td>
<td>clear</td>
</tr>
</tbody>
</table>

ppt – precipitation, AcA – acetic acid, diss. - dissolution

When Mo is precipitated using acetic acid, a cloudy solution can form overtime that can contain some portion of Mo. This very fine precipitate forms after centrifugation and can be filtered or let sit for some time and centrifuged again (Figure 9a). When a nitric acid wash is used, a very fine precipitate is formed (Figure 9b) that cannot be centrifuged or filtered (0.2μm filter). This fine precipitate can contain up to 15% of total Mo; however, when let sit for several hours, Mo losses are usually less than a few percent. After re-dissolving Mo precipitate in water and enough NH$_4$OH, Mo is precipitated again using acetic acid and washed multiple times with nitric acid. The Mo precipitate changes in color from white to yellowish when nitric acid is used for washing and the precipitate that forms after multiple washes with HNO$_3$ is soluble in water. This indicates formation of Mo-nitrate species rather than MoO$_3$. Speciation of Mo precipitate will be determined using XRD once final procedure is developed. Multiple experiments were performed using acetic acid, ethanol, and their mixture to precipitate molybdenum followed by acetic and nitric acid washes. Washes of acetic and nitric acid were allowed to sit for several hours, if cloudy solution formed. This helps significantly increase the recovery of Mo. Results from ICP-MS analyses of samples of Mo precipitated from K$_2$MoO$_4$ in 5M KOH solution using ethanol, and mixture of ethanol and acetic acid, followed by washing with acetic and nitric acid, show that ~99.995% of potassium can be removed after multiple washes with nitric acid. The concentration of K in final Mo product was ~100 ppm. However, the data for potassium are very close to the detection limit of instrument due to high concentration of Mo in samples, and are provided with high uncertainty. Very good Mo recovery, which was in the range of 97-100%, was observed. The fate of some selected metals that can form during irradiation or that are present...
as impurities, such as Fe, Zr, Nb, W, Al, Rh and Sb, without any designated purification step, was also investigated. W and Al are common Mo impurities and their starting concentration was ~400 and 100 ppm, respectively, other metals were added in 50 ppm concentration. W and Nb follow Mo quantitatively, while ~ 30-40% of Sb and 60-80% of Al was found in Mo precipitate. Concentrations of Zr and Rh in the final Mo product were below 2 ppm. 50 ppm of Fe that was added was below detection limit.

![Figure 9](image)

**Figure 9.** Mo precipitate after centrifugation. a) Precipitation with mixture of acetic acid and ethanol (left), and with acetic acid only (right). Cloudy solution containing Mo precipitate developed over time when only acetic acid was added. b) Cloudy solution containing Mo precipitate after washing precipitate with nitric acid and centrifugation.

4. **Conclusion**

It was demonstrated that mild pre-sinter, or no pre-sinter, and very strong sintering conditions usually lead to the disks with highest packing densities and lowest dissolution rates. On the other hand, stronger pre-sinter conditions and very mild sinter conditions lead to the higher dissolution rates. Dissolution rates and packing density of fast dissolving disks can be further optimized by using fine Mo powder (~400mesh) and increased pressing. Dissolution rates for disks with >92% density were ~0.6g/min, which is very good. Preliminary experiments for recovery of Mo from 0.2g-Mo/mL K₂MoO₄ in 5M KOH show that Mo can be effectively purified from large quantities of potassium using very simple process without significant losses in Mo recovery.

5. **References**


6. **Acknowledgment**

We would like to thank Steve Nunn of ORNL for providing optical micrographs of Mo sintered disks. Work supported by the U.S. Department of Energy, National Nuclear Security Administration’s (NNSA’s) Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.