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

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Accelerator Based Production of $^{99}\text{Mo}$

- ANL and LANL are assisting NorthStar in development of accelerator based production of $^{99}\text{Mo}$ through the $^{100}\text{Mo}(\gamma,n)^{99}\text{Mo}$ reaction.
- Enriched $^{100}\text{Mo}$ is commercially available for $\sim$ $1000$ per gram for kg quantities.
- High energy photons are created from a high power electron beam through bremsstrahlung.

$$Y_{m,E_0} = N_m \int_{E_{th}}^{E_0} \sigma_m(\gamma,n) \Phi_{E_0}(E)dE$$

- $N_m$ – atom density of material $m$
- $E_{th}$ – threshold energy in $m$
- $\Phi_{E_0}(E)$ – photon fluence spectrum
- $\sigma(\gamma,n)$ – cross section

Average bremsstrahlung photon spectra produced with 20- and 35-MeV electron beams in a Mo target compared to the photonuclear cross section of $^{100}\text{Mo}$. 
Molybdenum cycle

Disk production from Mo-100 powder

Mo recycled from 5M KOH to form MoO₃ and reduced to Mo

Mo-99 production by (γ, n) reaction

Target dissolution in H₂O₂ + KOH

0.2g-Mo/mL in 5M KOH in TechneGen generator

Target dissolution in H₂O₂ + KOH

Mo recycled from 5M KOH to form MoO₃ and reduced to Mo
Disks production

MoO₃ reduced by disk manufacturer to Mo powder and sintered

- Disks provided by NorthStar (also getting disks from ORNL)
- Every disk is characterized by a 3 digit code “ABC” e.g. “791”
  - A = powder treatment before pressing
  - B = disk pressing parameters
  - C = sinter conditions

Disk density determined from dimensions of the disks and divided by density of Mo metal (10.22g/mL)

GOAL: Find conditions for the production of Mo disks with high packing density (>92%) and good dissolution rates
Dissolution of Mo sintered disks in 30% H$_2$O$_2$

- $2\text{Mo(s)} + 10\text{H}_2\text{O}_2 = [\text{Mo}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-} + 2\text{H}_3\text{O}^+ + 5\text{H}_2\text{O}$
- Initial pH≈5, after dissolution pH ≈1-2
- 1 Mo disk ~1g, 40mL of 30% H$_2$O$_2$ at 70°C, H$_2$O$_2$:Mo molar ratio ~35

Auto-destruction of hydrogen peroxide to water and oxygen:

$$2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$$

After dissolution KOH added to make 0.2g-Mo/mL in 5M KOH

$$2[\text{Mo}_2\text{O}_3(\text{O}_2)_4(\text{H}_2\text{O})_2]^{2-} + 8\text{KOH} = 4\text{K}_2\text{MoO}_4\cdot(\text{H}_2\text{O})_2 + 5\text{O}_2$$
Effect of sinter conditions on density and dissolution

- Pre-sinter conditions A=0, 7, 9
- Pressing conditions B=4
- Sinter conditions C=1, 2, 7, 9

- Packing densities increase with stronger sintering conditions
- Stronger sinter “C” conditions lead to the lowest dissolution rates
- The best dissolving disks are with stronger pre-sinter (A=7-9) and weaker sinter conditions (C=1-2)
Effect of Mo powder size

- Pre-sinter conditions A=5, 7, 9
- Pressing conditions B=4
- Sinter conditions C=1, 2

<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>

- No significant effect on density for disks sintered at C=1, 2
- Disks made of finer particles (higher mesh) dissolve faster
Effect of Mo powder size

- Pre-sinter conditions A=7, 8, 9
- Pressing conditions B=4
- Sinter conditions C=6, 7, 8, 9

- Density increases with increasing “C”
- Dissolution rate decreases with increasing “C”
- -400 mesh disks dissolve faster than -20 mesh
Effect of pressing conditions cont.

- Pre-sinter conditions $A=7$
- Pressing conditions $B=8-11$
- Sinter conditions $C=1, 2, 6, 8$

packing densities for the disks with $C=1$: 90.7-92.6%
packing densities for the disks with $C=2$: 90.3-93.6%
packing densities for the disks with $C=6$: 89.4-94.7%
packing densities for the disks with $C=8$: 93-94.7%

diss. rates: ~0.6 g/min
diss. rates: ~0.4 g/min
diss. rates: ~0.28-0.14 g/min

diss. rates: ~0.16-0.08 g/min (heating)
Effect of pressing conditions cont.

“791” 4.9% Open Porosity

“792” 5.3% Open Porosity

“796” 3.8% Open Porosity

“798” 0% Open Porosity

Optical micrographs of “791”, “792”, “796”, and “798” disks provided by ORNL
**Dissolution - summary**

Dissolution rates of disks pre-sintered at A=7 and sintered at different conditions with densities ~92-94%

- Best dissolving disks are pre-sintered at higher temperature A=7-9 and sintered at C=1-2
- Densities for fastest dissolving disks (A=7-9, C=1-2) can be increased ≥92% by increased pressing parameter “B”
- Dissolution rates for disks with >90% density are mostly affected by “C” sintering conditions
Mo recovery

- Mo solution 0.2g-Mo/mL in 5M KOH: 1.8kg of K per 1kg of Mo
- Final product: ~25 ppm K – ~99.999% of K needs to be removed,
- >98% of Mo recovered

Purification from potassium

Mo in 5M KOH precipitated using glacial CH₃COOH, CH₃CH₂OH or their mixture (H₂SO₄ also tested)

- Small-scale experiments with 1-5 mL of K₂MoO₄
- EtOH precipitate Mo as K₂MoO₄
- more ppt forms with AcA – Mo-acetate interaction cloudy solution containing Mo develops over time
- EtOH + AcA – no ppt. over time
Mo recovery

<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>HNO₃</td>
<td>5-10%</td>
<td>0-15%</td>
<td>cloudy</td>
</tr>
<tr>
<td>diss. + ppt</td>
<td>H₂O+NH₄OH - AcA ppt</td>
<td>0-5%</td>
<td>0-3%</td>
<td>cloudy</td>
</tr>
<tr>
<td>wash 3</td>
<td>HNO₃</td>
<td>&lt;0.5%</td>
<td>0-15%</td>
<td>cloudy</td>
</tr>
<tr>
<td>wash 4</td>
<td>HNO₃</td>
<td>&lt;0.1%</td>
<td>0-2%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 5</td>
<td>HNO₃</td>
<td>&lt;0.1%</td>
<td>&lt;0.5%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 6</td>
<td>HNO₃</td>
<td>&lt;0.1%</td>
<td>&lt;0.5%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 7</td>
<td>HNO₃</td>
<td>&lt;0.1%</td>
<td>&lt;0.5%</td>
<td>clear</td>
</tr>
<tr>
<td>wash 8</td>
<td>HNO₃</td>
<td>&lt;0.1%</td>
<td>&lt;0.5%</td>
<td>clear</td>
</tr>
</tbody>
</table>

First 4 steps – 95-99% of potassium removed

99.9% purification – 1500 ppm of K

Optimizing Mo recovery – first washing steps are the most critical

Mo ppt formed after AcA – can be filtered

Mo ppt formed after HNO₃ - very fine – cannot be filtered (0.2μm)
Mo recovery - potassium analysis

Mo precipitate after final wash – dissolved and analyzed by K⁺ ISE, ICP-MS, ICP-OES

<table>
<thead>
<tr>
<th>Sample matrix</th>
<th>Detection limit for K</th>
<th>Issues</th>
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<tbody>
<tr>
<td>Mo</td>
<td>K</td>
<td>K⁺ ISE</td>
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<tr>
<td>8000 ppm</td>
<td>0.2 ppm</td>
<td>0.2-0.4 ppm</td>
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<tr>
<td>25 ppm K/Mo</td>
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</table>

<table>
<thead>
<tr>
<th>#</th>
<th>ppt</th>
<th>wash</th>
<th>wash</th>
<th>Diss.+ppt</th>
<th>Wash 5x</th>
<th>K ppm/Mo</th>
<th>Mo yield</th>
</tr>
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<tbody>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>A</td>
<td>EtOH</td>
<td>AcA</td>
<td>HNO₃</td>
<td>NH₄OH/AcA</td>
<td>HNO₃</td>
<td>K⁺ ISE</td>
<td>ICP-MS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>54 ppm</td>
<td>103 ppm</td>
</tr>
<tr>
<td>B</td>
<td>Ac/A/EtOH</td>
<td>AcA</td>
<td>HNO₃</td>
<td>NH₄OH/AcA</td>
<td>HNO₃</td>
<td>45 ppm</td>
<td>96 ppm</td>
</tr>
</tbody>
</table>

~99.997% of K removed
Mo recovery - summary and future plans

- Good Mo recovery **97-100%** obtained if HNO₃ washes allowed to sit for several hours
- Purification of potassium **<100 ppm** (99.997% removed) – work continues
- XRD characterization of Mo precipitate – converting to MoO₃
- Side products purification experiments upcoming
  
  Al, Zr, Nb, Rh, Sb (50 ppm/Mo), W (400 ppm/Mo)

**If no selective purification:**

- Nb and W follow Mo (100%)
- Al = 30-40 ppm (60-80%)
- Sb = <20 ppm (30-40%)
- Zr = ~1.4 ppm (2-3%)
- Rh = ~0.6 ppm (~1%)

**Possible purification options for side products**

- Precipitation after dissolution of Mo target
- Cation exchange
  - before loading into generator
  - during Mo recovery process
Acknowledgement

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