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Chemical Processing Activities for ^{99}Mo production by (γ, n) and (n, γ) reactions using enriched ^{100}Mo and ^{98}Mo targets

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ABSTRACT

Recently, several technologies were proposed for the production of $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ without the use of ^{235}U targets. These technologies offer the potential for a lower-cost alternative to fission produced ^{99}Mo , but with lower yields of ^{99}Mo or $^{99\text{m}}\text{Tc}$. Enriched ^{98}Mo or ^{100}Mo targets are necessary for economic production of several thousand Ci of ^{99}Mo . Argonne, in collaboration with Los Alamos and Oak Ridge National Laboratories, are assisting NorthStar Medical Technologies in the development of a domestic supply of ^{99}Mo . NorthStar's short-term plan is to produce ^{99}Mo using $^{98}\text{Mo}(n, \gamma)^{99}\text{Mo}$ reaction at MURR, and their long-term solution is to produce ^{99}Mo using an electron accelerator via the $^{100}\text{Mo}(\gamma, n)^{99}\text{Mo}$ reaction. The latest experimental results from irradiation of enriched ^{100}Mo targets, large-scale dissolution studies, and development of enriched material recycle process will be presented.

1. Introduction

Currently ^{99}Mo is produced by fissioning ^{235}U , but other technologies exist that don't require the use of ^{235}U such as: i) photonuclear reaction with photon source from bremsstrahlung $^{100}\text{Mo}(\gamma, n)^{99}\text{Mo}$ [1-7], or by $^{100}\text{Mo}(n, 2n)^{99}\text{Mo}$ using fast neutrons [8], ii) direct production of $^{99\text{m}}\text{Tc}$ in cyclotrons using $^{100}\text{Mo}(p, 2n)^{99\text{m}}\text{Tc}$ [9-13], or iii) neutron capture on ^{98}Mo [14-17] (Figure 1). All these alternatives offer a less-expensive alternative to fission-made ^{99}Mo , but with a lower yield. The main advantage of these alternative technologies is the minimum amount of low level waste generated due to very minimal purification requirements. However, in order to produce several kCi of ^{99}Mo , enriched ^{98}Mo or ^{100}Mo targets are required (enriched ^{100}Mo could be available for $\sim \$1000/\text{g}$ for kg quantities). One of the difficulties with production of low specific ^{99}Mo (high specific activity $^{99\text{m}}\text{Tc}$) is the need for a different generator designed to accommodate for the low specific activity of ^{99}Mo .

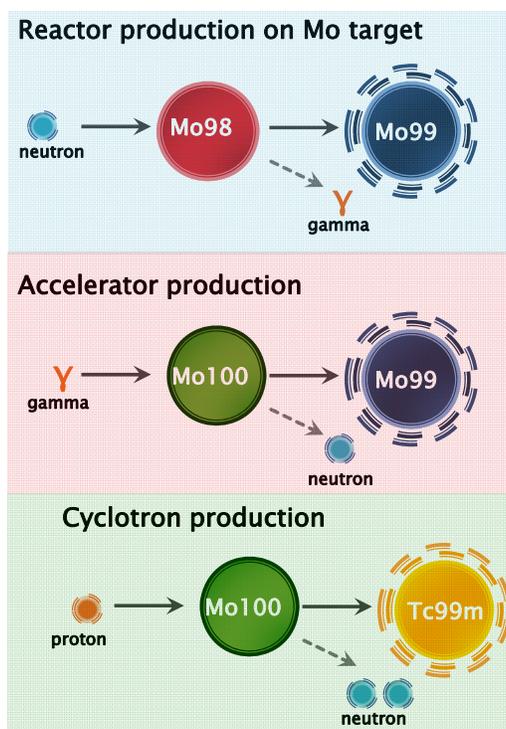


Figure 1. Various processes for production of ^{99}Mo without use of uranium target

Argonne National Laboratory (Argonne), in cooperation with Los Alamos (LANL), Oak Ridge National Laboratories (ORNL), and NorthStar Medical Technologies, LLC, is developing technology for the production of ^{99}Mo . As a short-term solution, NorthStar is planning to produce ^{99}Mo via $^{98}\text{Mo}(n, \gamma)^{99}\text{Mo}$ reaction at the University of Missouri Research Reactor (MURR), and, as a long-term solution, using the photonuclear reaction $^{100}\text{Mo}(\gamma, n)^{99}\text{Mo}$ produced from the irradiation of an enriched molybdenum target by an electron accelerator. In order to produce $\sim 1000\text{Ci}$ ^{99}Mo , the target is several hundred grams, and therefore processing requires fast dissolution kinetics. Argonne in collaboration with ORNL has been working on optimization of the production of Mo sintered disks for high theoretical packing density and fast dissolution kinetics. [18-20] NorthStar's RadioGenix[®] generator is designed for separation of $^{99\text{m}}\text{Tc}$ from low specific activity ^{99}Mo in highly alkaline solution. It uses ABEC resin, which is selective for Tc, while Mo passes through the column and is recovered for another separation. Due to the high cost of enriched Mo material (^{100}Mo or ^{98}Mo), the used generator solutions need to be recycled. One of the possible ways to recycle Mo that Argonne has developed, is the conversion of K_2MoO_4 in 5 M KOH solution into MoO_3 powder by precipitation of Mo from highly alkaline solution by acetic acid followed by washing with HNO_3 [21-23]. The MoO_3 product from the recovery process can be further reduced to MoO_2 and Mo metal with nearly quantitative recovery yields [20]. Here we discuss experimental results: i) from four ^{100}Mo enriched irradiations performed in FY15, ii) optimization of large-scale dissolution process, and iii) development of alternative recycle process using solvent extraction.

2. Experimental

2.1 Linac irradiations

Four production irradiations of Mo targets were performed in FY-15. After irradiation, the target was moved from the linac cell 1 into a hot cell for processing. Six ^{100}Mo enriched disks were dissolved in hydrogen peroxide; the remaining Mo disks were not dissolved. After complete dissolution, a saturated solution of KOH was added, the volume was adjusted by evaporation, and, after cooling, the solution was filtered through a $0.3\mu\text{m}$ filter and loaded into a shielded vessel that can be connected to NorthStar's RadioGenix[®] generator. Gamma counting was performed using an HPGe detector.

2.2 Large-scale dissolution of sintered Mo disks

Dissolution experiments of up to 300g of sintered Mo disks (provided by NorthStar) were performed in 30% and 50% hydrogen peroxide in a glass reaction vessel. Natural Mo disks ($26\times 1\text{mm}$) were dissolved in peroxide and repeatedly drained into an evaporation/concentration vessel. After complete dissolution, the dissolved Mo was evaporated to meet the required concentration $\sim 0.2\text{g-Mo/mL}$ as K_2MoO_4 in 5M KOH. After evaporation, the solution was filtered through a $0.2\mu\text{m}$ filter.

2.3 Alternative Mo recovery process

Small-scale solvent extraction experiments were performed to determine optimal conditions for effective extraction of high Mo concentrations. A solution of 50 % (by volume) tributyl phosphate (TBP) in 1-octanol or 30% TBP in tetrachloroethylene were used as the solvent for all extraction experiments. Before its use, the TBP was pre-equilibrated with an aqueous phase containing HCl in the same concentration as that used in the extraction experiment. Distribution ratios were measured in batch experiments; samples were rigorously agitated in extraction vials using a vortex mixer at a 1/1 organic/aqueous volume ratio under ambient temperature conditions (20°C). After agitation, phases were separated using centrifugation, and aliquots from both organic and aqueous phases were taken to measure equilibrium concentrations of the metal using NaI or HPGe detectors. Distribution ratios for experiments performed without ^{99}Mo tracers were determined using ICP-MS. Large-scale experiments were performed using 50% TBP in 1-octanol in 12L HDPE bottles and phases were separated using 5L separatory funnel.

3. Results and Discussion

3.1 Processing of irradiated enriched ^{100}Mo target

Four ~ 1 -day irradiations were performed using a target designed by LANL containing six ^{100}Mo enriched sintered disks, one ^{98}Mo enriched sintered disk (not in a direct beam path) and nineteen natural metallic Mo disks. The conditions for these irradiations are summarized in Table 1. After each irradiation, the Mo target was moved into a hot cell for processing. The disks were visually inspected, and it was noticed that some corrosion or dust occurs on disks placed from the middle towards the backend of the target. Figure 2 shows the photographs of all 26 disks from the 4th irradiation (see Table 1). Beam burn marks were

noticeable on the first five disks. The dust can also be seen on the target body (Figure 3). ICP-MS analysis revealed that the major component of the corrosion dust was Fe, which could possibly be coming from the gaseous He-cooling system. From each production test, six enriched disks were dissolved in 50% hydrogen peroxide using the apparatus shown in Figure 4. After complete dissolution, KOH was added to make K_2MoO_4 in KOH. The solution was further evaporated to adjust the volume to meet the required concentration of Mo (0.2g-Mo/mL) and 5M KOH. The solution was then filtered through a $0.3\mu m$ filter and loaded into a NorthStar shielded container for the Mo/Tc separation.

Table 1. Conditions for four production tests using six ^{100}Mo enriched disks performed in FY15

^{100}Mo (position)	^{99}Mo in 6 disks, Ci	Power, kW	Current, μA	Time, hrs.	Energy, MeV
99% (1-6)	0.92	4	95	19	42
97.4% (3-8)	2.9	7.56	180	21	42
95.1% (3-8)	2.2	7.56	180	19	42
99% (3-8)	4.2	7.77	222	24.4	35

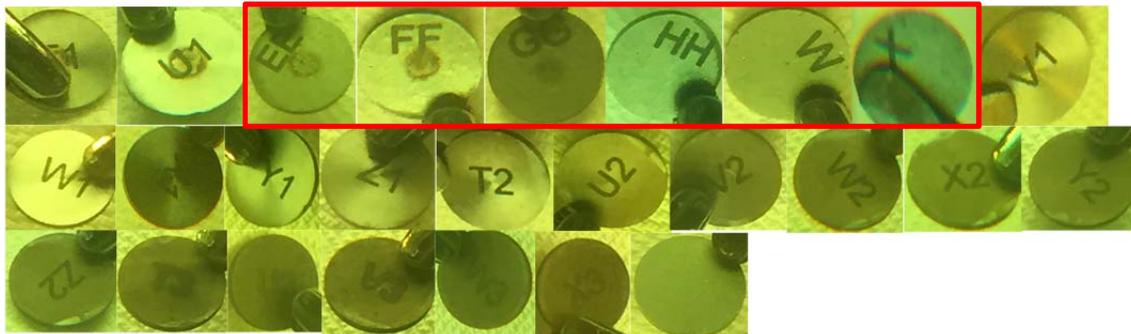


Figure 2. Photographs of 26 disks used in 4th irradiation (see Table 1). Highlighted disks are ^{100}Mo enriched disks; the last disk on the bottom right is ^{98}Mo enriched disk



Figure 3. Dust observed on the target body and natural Mo disks



Figure 4. Dissolution apparatus used for dissolution of six ^{100}Mo enriched disks

All natural disks from the 1st irradiation were also gamma counted to confirm the distribution profile of ^{99}Mo activity within the target. The experimental results compared with calculated data obtained from MCNPX calculation are shown in Figure 5. Since the correlation between experimental and calculated ^{99}Mo activity distribution was very good, the natural disks from the next irradiations were not gamma counted.

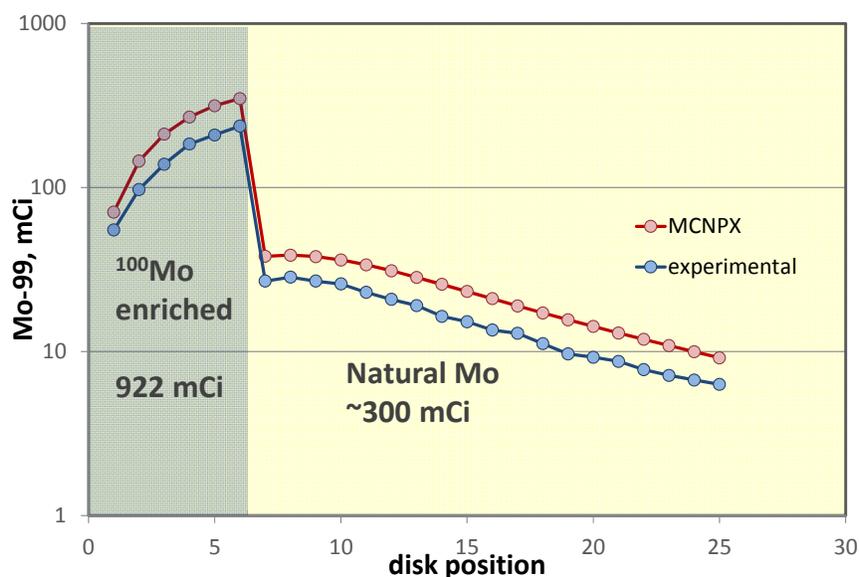


Figure 5. Correlation between experimental and theoretical distribution of ^{99}Mo in the target containing six ^{100}Mo enriched and 19 natural Mo disks

The solution from the first production run was loaded onto the TechnGen generator; however, low and inconsistent yields for $^{99\text{m}}\text{Tc}$ were observed. The dissolved targets from 2nd-4th irradiations were sent to NorthStar for processing with RadioGenix, but similar results were observed. These inconsistencies were attributed to the impurities in the solution, and Argonne is currently working on resolving this issue.

3.2 Large-scale dissolution processing

Three ~75g batches of sintered Mo disks (NorthStar) were dissolved in a 2L reaction kettle (Figure 6A) using 50% H₂O₂ and one ~75g batch (ORNL) was dissolved in 30% H₂O₂. All three batches dissolved in ~30min, independent of the hydrogen-peroxide concentration or source of the Mo disks. No additional heating was provided. Dissolution was performed by the addition of H₂O₂ aliquots to a vessel containing 75g of Mo disks, and all vapors were exhausted into the ventilation system. As the dissolution proceeded, the solution turned yellow and then orange in color. The orange-colored solution was transferred into the evaporation/concentration vessel and a fresh portion of H₂O₂ was added to continue the dissolution.

After a complete dissolution and transfer of the solution to the evaporation vessel, the remaining H₂O₂ was destroyed by heating and KOH was added to make a solution of ~0.2g-Mo/mL in ~5M KOH. Total processing time for disks dissolved in 50% H₂O₂ was ~2hrs and 1hr 40min, respectively, while the total processing time for disks dissolved in 30% H₂O₂ was ~4hrs. Larger volume of 30% H₂O₂ was required to completely dissolve the disks, and therefore the evaporation/concentration step was significantly longer.



Figure 6. Setup used for dissolution of 75-300g of sintered Mo disks using 30-50% hydrogen peroxide

For the processing of 300g of Mo disks, the dissolution was performed in a ~5L reaction kettle with a small frit (Figure 6B) and drain on the bottom to remove the dissolved portion of Mo into the concentration vessel using vacuum. However, the small frit was clogged very easily by undissolved Mo-disk material and significantly slowed down the dissolution process. The reaction vessel was modified by adding a larger frit (Figure 6C). Also, two additional condensers were added to decrease the amount of vapors released during the dissolution. Large-scale dissolution tests are summarized in Table 2.

Table 2. Summary of large-scale dissolution tests

#	H ₂ O ₂ , %	diss. vessel, L	Mo, g	dissolution, hrs	evaporation, hrs	total, hrs	concentration step
1	50	2	75	0.5	1.5	2	open to atmosphere
2	50	2	75	0.5	1.2	1.7	open to atmosphere
3	30	2	75	0.5	3.5	4	open to atmosphere
4	50	5	300	2	5.8	7.8	vacuum
5	50	5	300	2.7	6	8.7	vacuum
6	50	5	300	2	6.8	8.8	vacuum
7	30	5	300	1.4	6.4	7.8	vacuum

3.3 Alternative Mo recovery process

Recovery of enriched ⁹⁸Mo or ¹⁰⁰Mo using a solvent extraction process has several advantages. It can be fully automated by countercurrent flow through a centrifugal contactor; very high separation factors can be obtained. A tributyl phosphate (TBP)/hydrochloric acid system can handle high concentration of Mo (~0.5M Mo) with very high extraction yields, while potassium stays in the aqueous phase. The traditional diluent used with TBP is n-dodecane, however 3rd phase formation at higher HCl concentrations prevents its use with centrifugal contactors. 1-octanol or tetrachloroethylene (TCE), on the other hand, are suitable diluents for this process. Figure 7 shows the distribution ratios of Mo for TBP/HCl system using these diluents.

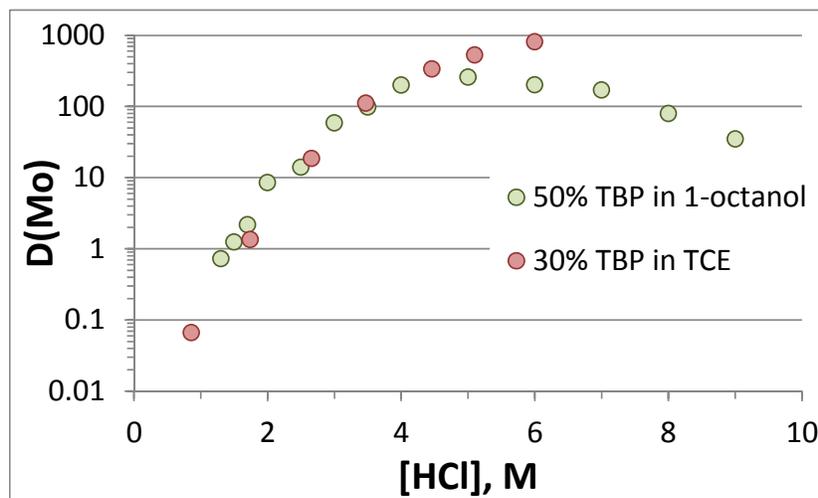


Figure 7. Distribution ratios of trace Mo between TBP and HCl

Distribution ratios from 5M HCl for potassium are very low with a separation factor of $SF_{(Mo/K)} \sim 1E4$ for one stage of extraction. After extraction step, any impurities present in the organic phase are scrubbed with HCl and then Mo is stripped from the organic phase using NH_4OH . A flowsheet of the recovery process using solvent extraction is illustrated in Figure 8.

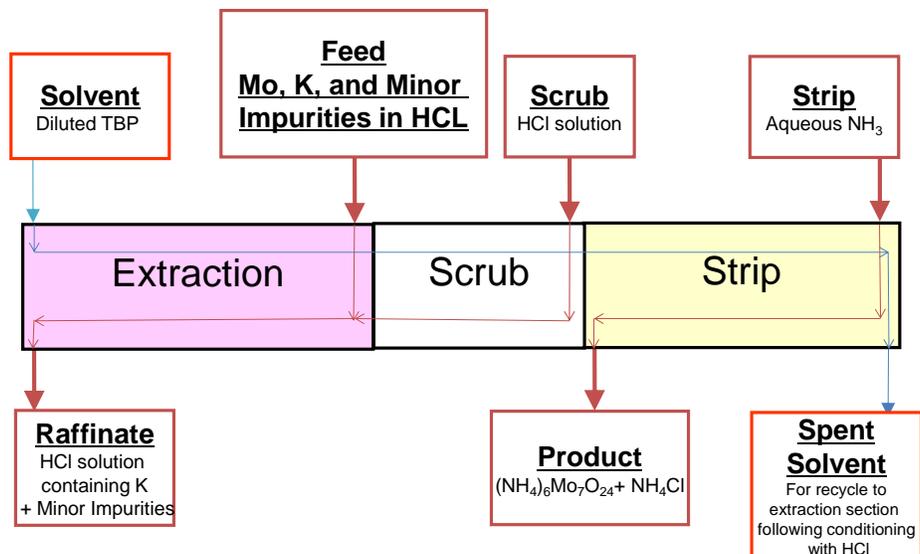


Figure 8. Flowsheet diagram of Mo recovery process using solvent extraction with TBP

The Mo-product solution (a mixture of NH_4Cl and $(NH_4)_6Mo_7O_{24}$ in NH_4OH) is concentrated using evaporation and treated to remove NH_4Cl . Several options were investigated. One of them is removing NH_4Cl by sublimation at $\sim 340^\circ C$ (Figure 9A) while ammonium molybdate is decomposing and forms MoO_3 at $\sim 360^\circ C$. Another option is precipitation of Mo from the alkaline strip solution using acetic acid (AcA). Ammonium chloride stays in the solution, while Mo can be collected by filtration, washed with acetic acid and then with ethanol. Dried white Mo precipitate (Figure 9B) is then heated at $500^\circ C$ and converted to MoO_3 (Figure 9C).

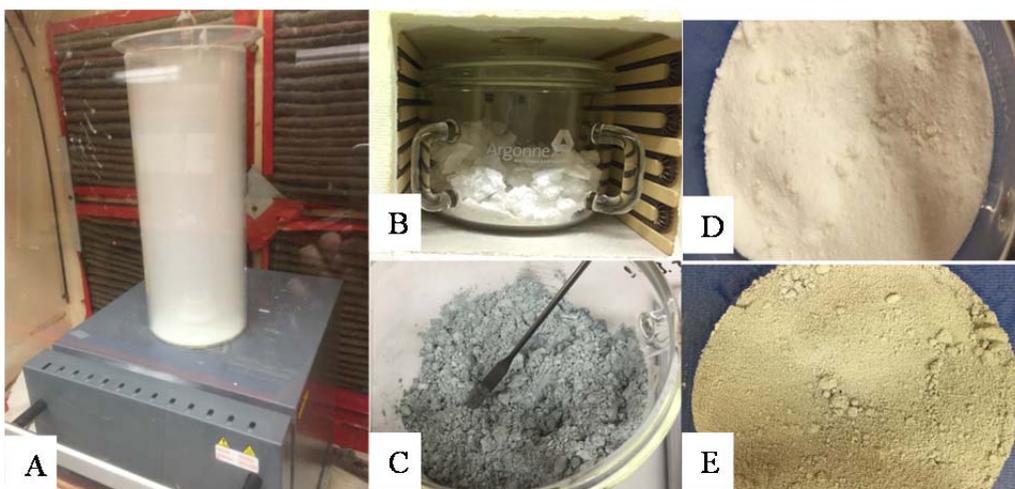


Figure 9. Photographs of A) sublimation of NH_4Cl , B) white solid obtained after Mo precipitation with AcA and C) MoO_3 product after heating, D) ammonium molybdate obtained after wash with ethanol-water mixture, and E) MoO_3 product obtained after heating

A third option is differential solubility in an ethanol-water mixture. NH_4Cl is more soluble in an ethanol-water mixture compared to an ammonium molybdate. If a solid mixture of NH_4Cl and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ is washed several times with an ethanol-water mixture, the NH_4Cl is dissolved and removed while the ammonium molybdate remains as a solid on a filter. Figure 9D shows recovered ammonium molybdate and Figure 9E MoO_3 product after heating at 500°C .

Several large-scale experiments using 700mL of spent generator solution surrogate with 0.2g-Mo/ml in $\sim 5\text{M}$ KOH solution were performed. After acidification with concentrated HCl, about 30-40% of potassium precipitates as KCl due to limited solubility of KCl in HCl. The solution was cooled to room temperature and filtered. Mo in HCl was contacted with 50% TBP in 1-octanol, scrubbed and stripped as shown in Figure 8. Usual recovery yields obtained were $\sim 98\%$ and concentration of K $< 200\text{ppm}$ after single extraction step. $\sim 500\text{g}$ of recovered Mo material was sent to ORNL for reduction to Mo metal and production of sintered Mo disks.

4. Conclusions

Argonne is assisting NorthStar in developing processing methods that will be applicable for producing ^{99}Mo through either n,γ or γ,n reactions on enriched-Mo targets. Development activities have taken the processes from bench-scale to production-scale.

5. References

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