SCALABILITY OF THE LEU-MODIFIED CINTICHEM PROCESS

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ABSTRACT

Argonne National Laboratory with the National Nuclear Security Admiration's (NNSA) Material Minimization and Management program (M^3), in partnership with SHINE Medical Technologies are developing technologies for the domestic production of [99]Mo. SHINE is planning to produce [99]Mo by fission of low enriched uranium (LEU) in a subcritical aqueous solution using an accelerator-based neutron generation. In support of this goal, irradiations at Argonne's Van-de-Graaff facility simulating LINAC irradiations were performed. The LEU-Modified Cintichem process has been chosen by SHINE to process their irradiated solutions. However, Cintichem rarely processed more than 1000 Ci of [99]Mo in a single batch. A concern is the Mo-ABO complex will break down under high dose conditions, causing a decrease in the recovery of [99]Mo. Irradiations of the Mo-ABO solid have been performed and the results will be discussed.

1. Introduction

The Cintichem process has been modified for the purification of [99]Mo from LEU targets (the LEU-Modified Cintichem process—LMC), and LMC has been chosen by SHINE to process their irradiated solutions [1,2]. Cintichem rarely processed more than 1000 Ci of [99]Mo in a single batch. In this process, Mo(VI) is precipitated by α-benzoin oxime (ABO, Figure 1), a standard analytical method for molybdenum quantification [3,4-8]. ABO is the key reagent of the Cintichem and LMC process, allowing for selective precipitation of molybdenum from acidic solutions (~1 M HNO_3), where molybdenum is present as molybdenyl cation (MoO_2^{2+}).

A concern is that ABO will break down under high dose conditions causing a decrease in the recovery of [99]Mo. Previous experiments performed at Argonne National Laboratory determined the adsorbed dose that ABO-precipitated molybdenum could tolerate from [99]Mo without causing losses of Mo was over 28,000 Ci when dry or 7,000 Ci when in contact with nitric acid. The experiments were performed by direct irradiation of small samples in test tubes with an electron beam. Samples were placed directly next to the Van de Graaff (VDG) beam exit window and irradiated for various time lengths at set beam parameters. A narrow beam and beam

"wandering" introduced errors in perceived doses, so these experiments have been repeated using a wider beam. A wider beam allowed for a more uniform irradiation zone and thus uniform dose even if beam "wandering" occurs.
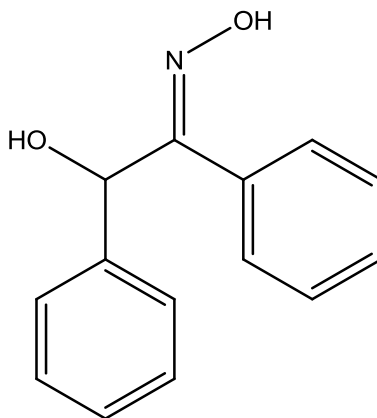

FIGURE 1. α-benzoin oxime (ABO)

Computational studies have also been conducted at Argonne to determine the absorbed dose in ABO during the actual processing time of this step in the LMC from 1 kCi of ^{99}Mo. Simulations with the Monte Carlo N-Particle Transport Code (MCNPX) [9] were conducted under several conditions and provided a link between ^{99}Mo activity and the dose received by the Mo-ABO complex. For a more conservative scenario when the Mo-ABO precipitate was present as a monolayer, Makarashvili et al. determined that the precipitate will receive a dose of 148.3 Mrad/kCi ^{99}Mo [9].

Experimental determination of the dose received by the sample required a dosimeter of identical geometry. Draganic reported that oxalic acid can be used as a dosimeter in aqueous solution and is the only dosimeter available for reactors [10]. Other aqueous chemical dosimeters exist, but oxalic acid holds advantages over them, such as 1) higher dose limits, 2) no activation of dosimeter, and 3) insensitivity to impurities and absence of photosensitivity. Oxalic acid will decompose with irradiation and the dose is determined by comparing the concentration of acid prior to and after irradiation. Residual acid is then determined through titration analysis with NaOH. Once the concentration of acid is determined, the dose can be calculated from the following equation [10].

$$\text{Log}(D) = a \log(C) + b \qquad \text{Eq. 1}$$

where D = absorbed dose in eV/mL; C = number of oxalic acid molecules decomposed in 1 mL; and a and b are constants dependent on the initial concentration of oxalic acid and the number of moles of oxalic acid decomposed, found in Table 1.

TABLE 1. Equations for Calculating Dose

Initial (COOH)$_2$ Concentration (M)	Range of log (C)	Dose Equation
25	18.380 < log(C) < 18.676	log(D) = 0.999 log (C) + 1.344
	18.676 < log(C) < 19.057	log(D) = 1.512 log (C) - 8.244
50	18.380 < log(C) < 18.954	log(D) = 0.999 log (C) + 1.344
	18.954 < log(C) < 19.373	log(D) = 1.426 log (C) - 6.774
100	18.380 < log(C) < 19.230	log(D) = 0.999 log (C) + 1.344
	19.230 < log(C) < 19.663	log(D) = 1.295 log (C) - 4.359
600	18.380 < log(C) < 19.978	log(D) = 0.999 log (C) + 1.344
	19.978 < log(C) < 20.505	log(D) = 1.400 log (C) - 6.668

The scalability of the LMC is being determined in two stages: Stage I – Van de Graaff (VDG) irradiations; Stage II – Electron linac irradiations. Stage I irradiated small scale targets containing Mo-ABO solid covered by HNO$_3$ (0.1 M) using a 3 MeV VDG accelerator (with a wide beam to eliminate random errors due to differences in beam alignment) and verification of earlier results. Stage II will more closely simulate actual processing with use of electron linac irradiations. This includes remotely washing the Mo-ABO solid with HNO$_3$ (0.1 M) during ~20 minute irradiations. Stage I has been completed and Stage II is underway.

2. Experimental

2.1. Stage I: Van de Graaff Irradiations

To achieve a uniform dose across the sample and eliminate beam "wandering," the sample was placed 15 in. from the beam window. Laser levels were used to position the apparatus built for this experiment (Figure 2). The sample was centered in the middle of the beam path and cooled with a stream of chilled compressed air. Under radiological conditions (the use of tracer [99]Mo), the rig needed to be enclosed and exhausted through a HEPA filter. The beam current was read on the beam shutter before irradiation of the sample and correlated with the current on the sample holder. During irradiation, the current was monitored on the aluminum sample holder, allowing for real-time beam current readout.

Beam profiles were performed at 10 in. and 15 in. from the window using a faraday cup. The faraday cup was centered on the beam and then moved from the center in half-inch increments to obtain a profile. The results are summarized in Figure 3. It can be seen that a one-inch radial uniform beam can be achieved 15 in. from the beam shutter window.
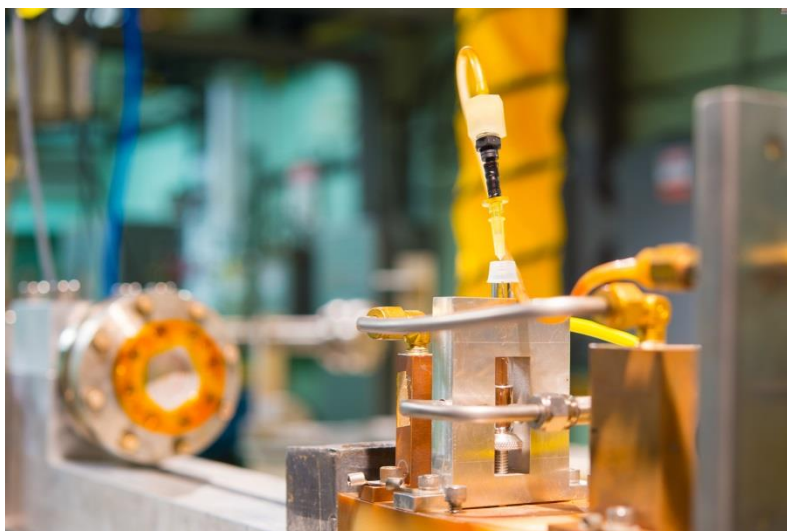
FIGURE 2. Rig for Mo-ABO Dose Experiment. The sample is located in the aluminum block with the beam window to the left. The sample holder was placed on a rail system allowing samples to be irradiated at different distances. Compressed air was passed through an ice bath to cool the samples. A copper beam stop is located behind the sample.
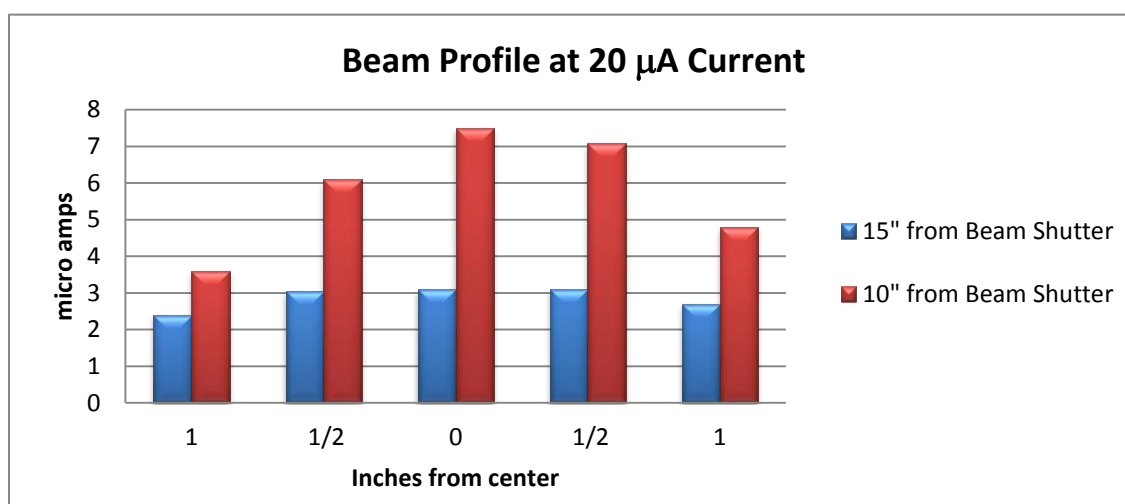

FIGURE 3. Plot of VDG Beam Profile at 10 in. and 15 in. from Beam Shutter Window with 20 μA Current

The temperature of the sample will increase with irradiation to the point at which the solution will boil or a solid will burn. Therefore, the sample temperature was monitored with a thermocouple to obtain a temperature profile. Molybdenum was precipitated with ABO, isolated, covered with HNO_3, and used to obtain a temperature profile prior to the actual sample irradiation. A thermocouple was immersed in the Mo-ABO sample in HNO_3 (0.1 M, 200 μL). To prevent boiling of the solution, the sample needed to be cooled. A copper coil was attached to the compressed air lines and submerged in a salted ice bath prior to passing a stream of air through the coil and over the sample. The temperature of the sample with cooling in this manner reached ~43±2 °C after ~30 min and did not change significantly over time. For longer irradiations, the

salted ice bath was replaced as necessary. During irradiation, the temperature of the sample was externally monitored by a thermocouple placed in contact with the exterior of the irradiated vial. The results of temperature profile are summarized in Figure 4. Note that the temperature readings from the external thermocouple touching the sample (triangles) are lower than those from the thermocouple immersed in the sample (circles) because it was in the direct stream of the cooling air.
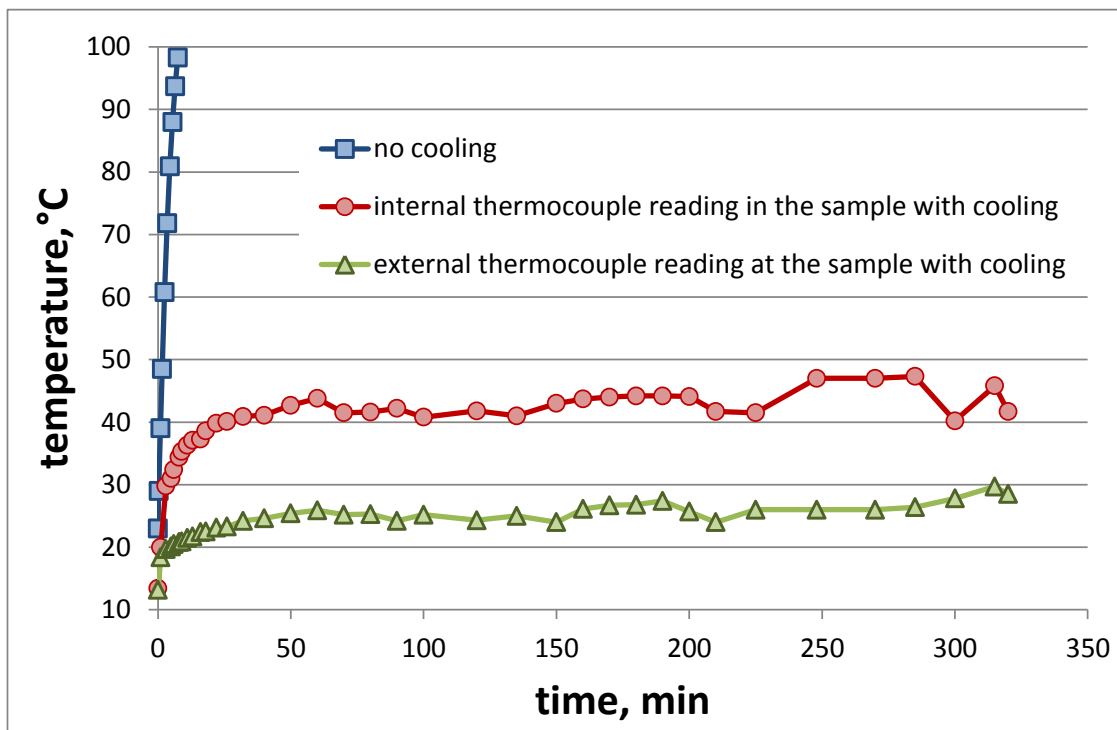

FIGURE 4. Temperature Profile of sample during trial irradiations

Doses were determined by oxalic-acid dosimetry. A solution of oxalic acid (~0.6 M, 1 mL) was irradiated with various beam currents at 15 in. from the window for various time lengths and cooled with a constant stream of compressed air (chilled by a salted ice bath). The clear glass test tube browned over time. Irradiated solutions of oxalic acid (0.9 mL) were titrated with standardized NaOH to determine the final concentration of oxalic acid. Plotting the results yielded a linear dose curve (Figure 5). It is important to realize that the dose is extremely dependent on the position of the sample. Even slight variations in the sample's position will dramatically alter the dose received. Therefore, it is beneficial to perform dose calibrations with the apparatus in the position in which the experiment will be conducted.
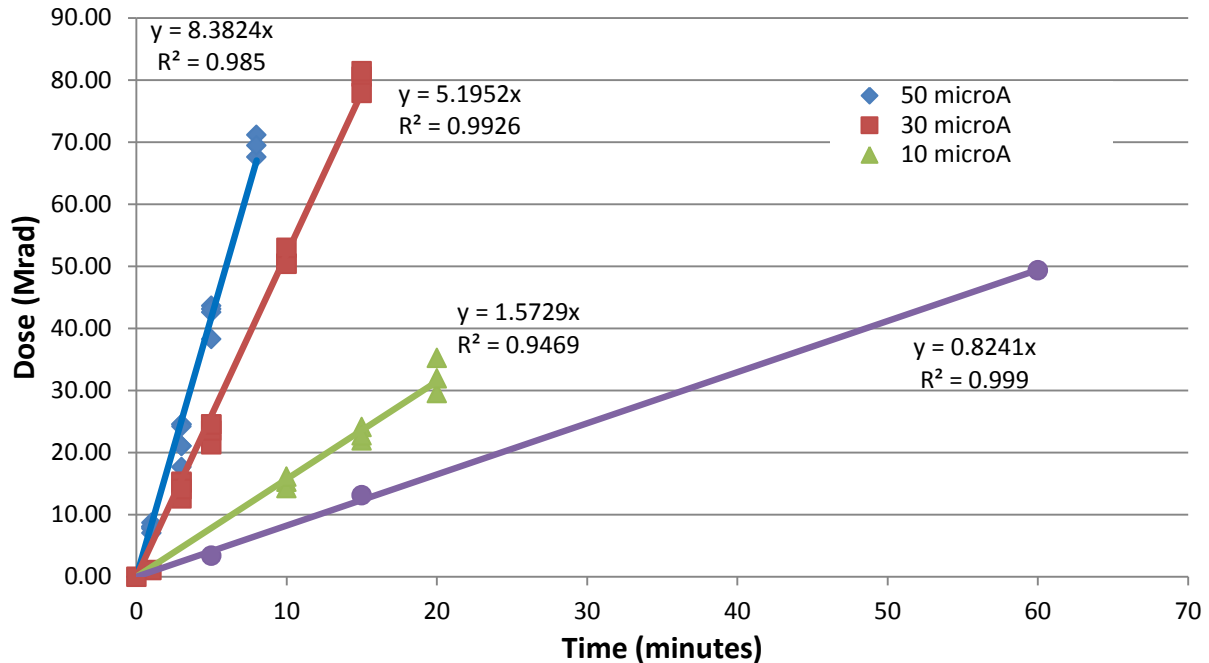
FIGURE 5. Oxalic Acid Dosimetry calibration curves at 15 in. from beam window at various beam currents

Molybdenum-ABO irradiations were performed after complete profiling the beam and oxalic acid dosimetry measurements. A molybdenum carrier solution (10 mg-Mo/mL) was prepared by dissolving MoO_3 in NaOH (1 M) and neutralizing it with HNO_3 (8 M). Prior to precipitation with ABO, the Mo carrier solution was spiked with a known amount of [99]Mo. The ABO (2%) was prepared by dissolution in hot NaOH (0.4 M). A Mo carrier (11.0 μL) spiked with [99]Mo was diluted with HNO_3 (~1.43 M, ~1.47 mL) and oxidized with $KMnO_4$ (2.5 % $KMnO_4$, 68 μL). The resultant solution was mixed and then precipitated with the ABO stock solution (453 mL). The mixture was centrifuged, and the supernatant was removed. The Mo-ABO solid was covered with HNO_3 (0.1 M, 200 μL) and irradiated in a glass vial.

After irradiation, the samples were filtered with a 0.22-μm polyvinylidene fluoride (PVDF) membrane filter (Millipore). The vessel and filter were washed with HNO_3 (0.1 M, 2.0 mL). The wash was kept for gamma analysis. The Mo-ABO precipitate was dissolved from the filter using a hot NaOH/H_2O_2 solution (0.4 M NaOH, 1 % H_2O_2, 1.5 mL). To ensure complete dissolution of the ABO-Mo precipitate, the filter was washed with an additional NaOH/H_2O_2 (0.2 M NaOH, 1 % H_2O_2, 1.0 mL). Another NaOH wash (0.2 M, 0.5 mL) was used to rinse any remaining residue left on the filter. All NaOH fractions were collected, combined, and kept for gamma analysis. A high purity germanium (HPGe) gamma detector was used to determine the amount of [99]Mo (739.4 keV emission) in the HNO_3 wash, NaOH product, and any remaining on the filter.

2.2. Stage II: Electron Linac Irradiations

Stage II will more closely simulate the actual LMC processing, including the entire series of washes, in a system that closely represents the actual process. In a hot cell, this step of the LMC generally takes 20 minutes to complete. Therefore the 8 wash steps will be performed remotely during 20 minute irradiations. Beam parameters such as current and power will be adjusted to obtain dose rates similar to those achieved during Stage I.

In order to achieve uniform dose throughout the full-scale sample, the apparatus required rotation relative to the incident beam (Figure 5). A vertical shaft with prongs holds the sample in line with the beam and will be rotated by a motor affixed to an adjustable mounting plate. A syringe pump, loaded with HNO_3 (0.1 M) will deliver the desired volume of solution for each wash step and a diaphragm vacuum pump will remove the solution. The flow of solution is controlled by two valves. The washes will be combined and analyzed to determine the amount of Mo lost to the washes. Residual Mo-ABO solid will be dissolved and analyzed to determine the amount of Mo left in the solid phase. The system has been tested and linac irradiations are scheduled.
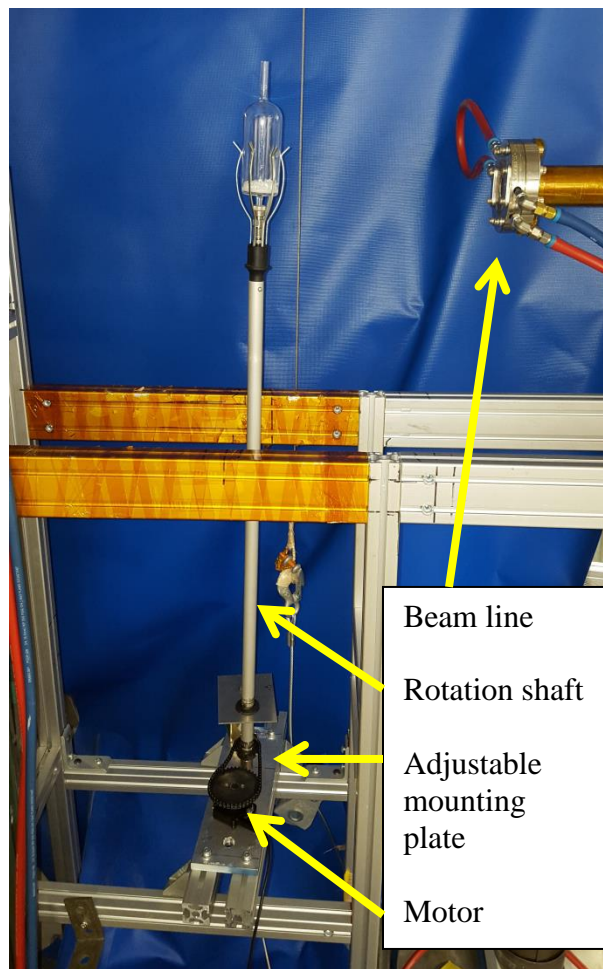

FIGURE 5. Mo-ABO linac apparatus

3. Results and Discussion

Freshly prepared samples of Mo-ABO precipitate in the presence of HNO$_3$ were irradiated with a 3 MeV electron beam with a current of 50 μA and received doses in the range of 254 – 4156 Mrad. After irradiation, a significant change in color was observed for the precipitate (Figure 6c). It was found that freshly prepared Mo-ABO solid was able to withstand greater doses than samples prepared 24 hrs in advance, this has been attributed to the morphology of the solid (Figure 6A and B). The data in Table 2 and Figure 7 show the distribution of ^{99}Mo in the HNO$_3$ wash, NaOH product solution, and on the filter.
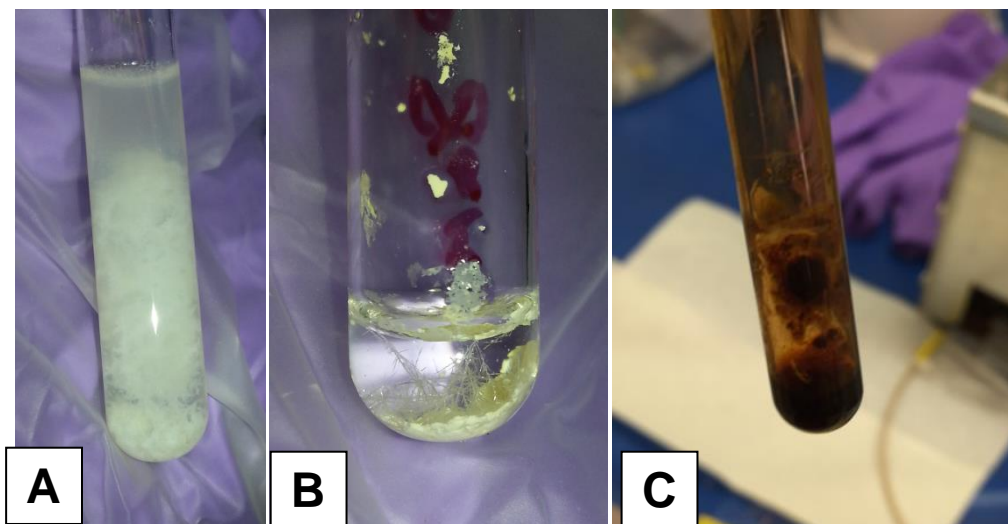

FIGURE 6. Samples of Mo-ABO Precipitate A) directly after solid formation, B) 24 hours after solid formation, and C) after receiving rose of 340 Mrad

TABLE 2. Distribution of ^{99}Mo in 0.1M HNO$_3$ Wash, in NaOH Product Solution, and on Filter

Sample #	Dose (Mrad)	kCi of ^{99}Mo	^{99}Mo Distribution (%)		
			HNO$_3$	Filter	NaOH
1	254.02	1.71	2.70	8.54	100.33
2	570.48	3.85	8.19	1.07	96.42
3	1006.34	6.79	11.35	12.14	91.05
3*	1068.60	7.20	47.66	4.35	57.10
4	1581.94	10.67	13.39	4.47	86.57
5	2588.64	17.46	25.39	4.28	82.57
6	3180.15	21.44	42.91	1.72	59.12
7	3600.60	24.28	91.21	---	12.10
8	4156.48	28.03	81.84	---	24.61

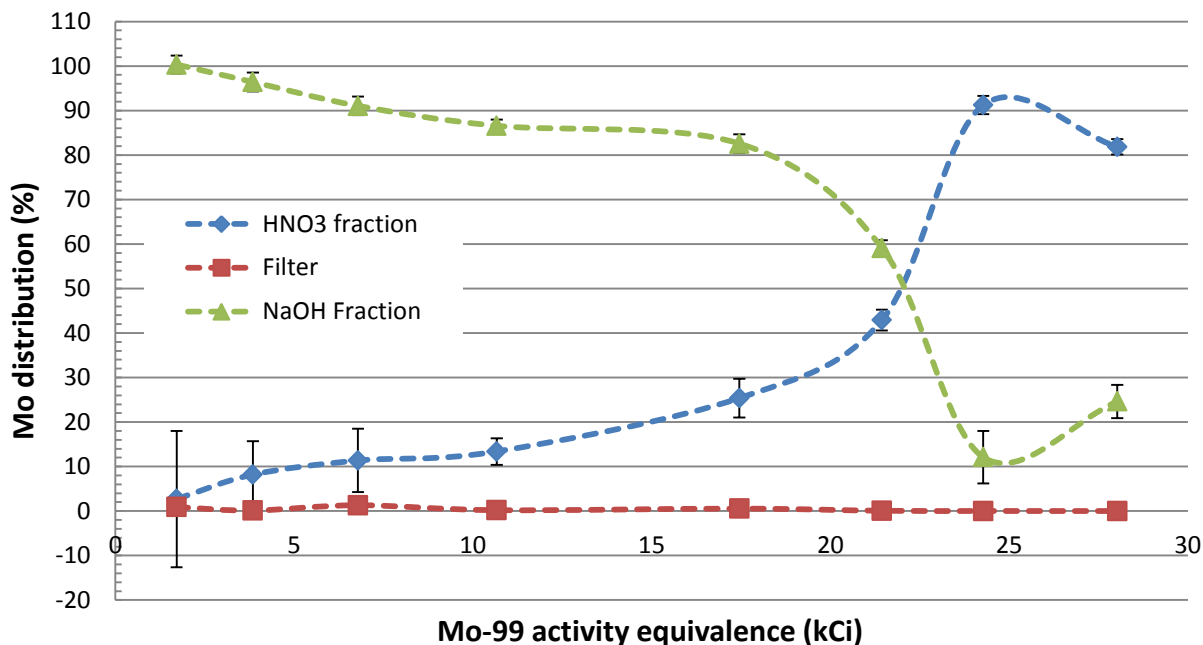*sample was prepared 24 hrs prior to irradiation, not shown in Figure 6

FIGURE 7. Mo Recovery Results for Mo-ABO Irradiations in Presence of 0.1 M HNO₃

All samples exhibited signs of degradation after irradiation; colorless to light yellow Mo-ABO was darkened if not blackened, colorless HNO_3 turned a light yellow color after washing irradiated Mo-ABO, and the NaOH Mo-ABO solutions were dark brown. Despite the discoloration of the HNO_3 wash, only a small portion of Mo was detected in this fraction at low doses. Larger fractions of Mo were observed in these washes at doses >1500 Mrad (>10 kCi [99]Mo equivalent). From the data in Table 2 and Figure 7, it is evident that at doses >1500 Mrad, the decomposition of the Mo-ABO complex leads to the formation of Mo species that are soluble in 0.1 M HNO_3, which causes a noticeable decrease in Mo recovery. Previously obtained data [11] using a narrower beam showed a noticeable degradation of the Mo-ABO complex and increased Mo content in the HNO_3 wash at the dose equivalent to ~7.5 kCi of [99]Mo. Greater than 25% loss of Mo was achieved with doses equivalents >17 kCi of [99]Mo and nearly complete degradation was observed with doses equivalents >24 kCi of [99]Mo.

4. Conclusions

Irradiation of the Mo-alpha-benzoin oxime (Mo-ABO) precipitate spiked with [99]Mo was performed at a Van de Graaff accelerator using a wide electron beam at 15 in. from the window. Samples of the Mo-ABO precipitate in a glass vial were irradiated in the presence of HNO_3 and cooled by a jet of cold compressed air. The temperature of the sample during irradiation was ~43 °C. Dose equivalents up to 29.03 kCi of [99]Mo were applied. After irradiation, the Mo-ABO precipitate was filtered, washed with HNO_3, dissolved in a hot $NaOH/H_2O_2$ mixture, and rinsed with NaOH. All washes, dissolutions, and rinses were gamma counted to determine [99]Mo content. The experimental data demonstrate good radiation stability (<10% losses) of the Mo-ABO complex up to ~10 kCi dose equivalents of [99]Mo. At higher doses, the decomposition of the Mo-ABO complex leads to the formation of Mo species that are soluble in HNO_3 (>10%) and causes a noticeable decrease in Mo recovery. A system has been developed and built for Stage II

with rotation and fluid delivery/removal capabilities. Stage II experimentation is currently underway.

5. References

1. A.J. Youker, D.C. Stepinski, L. Ling, N-H.L. Wang, G.F. Vandegrift, "Column Optimization for Mo Separation and Recovery", *Proceedings of the [99]Mo Topical Meeting on Molybdenum-99 Technological Development*, Washington DC, USA, June 24-27, **2014**, S9-P9
2. D.A. Rotsch, A.J. Youker, P. Tkac, D.C. Stepinski, J.F. Krebs, V. Makarashvili, M. Kalensky, Z. Sun, T.A. Heltemes, J.F. Schneider, A.S. Hebden, J.P. Byrnes, L. Hafenrichter, K.A. Wesolowski, S.D. Chemerisov, G.F. Vandegrift, "Chemical Processing of mini-SHINE Target Solutions for Recovery and Purification of [99]Mo", *Proceedings of the [99]Mo Topical Meeting on Molybdenum-99 Technological Development*, Washington DC, USA, June 24-27, **2014**, S9-P8
3. D. Wu, B. A. Buchholz, S. Landsberger, G. F. Vandegrift, "Processing of LEU Targets for Mo Production–Testing and Modification of the Cintichem Process," Proceedings of the XVIII International Reduced Enrichment for Research and Testing Reactors Meeting, Paris, France, September 17-21, 1995, paper no. 3-3, May **1996**.
4. Vandegrift, G. F.; Conner, C.; Hofman, G. L.; Snelgrove, J. L. (ANL); Mutalib, A.; Purwadi, B.; Adang, H. G.; Hotman, L.; Moeridoen, K.; Sukmana, A.; Dicky, T. J.; Sriyono, A.; Suripto, H.; Nasution, D. L.; Amin, A.; Basiran, A.; Gogo, S.; Taryo, T. (PUSPIPTEK) "Demonstration of [99]Mo Production Using LEU Metal-Foil Targets in the Cintichem Process". *Proceedings of the 22nd International Meeting on Reduced Enrichment for Research and Test Reactors*, Budapest, Hungary, Oct 3−8, **1999**.
5. D. Wu, S. Landsberger, G. F. Vandegrift, "Application of Neutron Activation Analysis in a Fission Molybdenum Separation Study," J. Radioanal. Nucl. Chem., in press, **1996**.
6. A. Elwell, Analytical Chemistry of Molybdenum and Tungsten, Pergamon Press, Oxford, New York, **1977**, pp. 40-41.
7. A. Parker, Analytical Chemistry of Molybdenum, Springer-Verlag, Berlin, New York, **1983**, pp. 146-147.
8. C. Conner, M. W. Liberatore, A. Mutalib, J. Sedlet, D. Walker, G. F. Vandegrift, "Progress in Developing Processes for Converting [99]Mo Production from High- to Low-Enriched Uranium--1998,"*1998 International RERTR Meeting*, Sao Paulo, Brazil, **1998**
9. V. Makarashvili, S. Chemerisov, P. Tkac, G. F. Vandegrift, S. Zaijing, K. J. Quigley, G. Van-de-Graaff, "Dose Rate Calculations Irradiations for Testing Radiation Stability of Materials and Equipment", *Proceedings of the [99]Mo Topical Meeting on Molybdenum-99 Technological Development*, Washington DC, USA, June 24-27, **2014**, S9-P5
10. I. Draganic, Oxalic Acid: The Only Aqueous Dosimeter for In-Pile Use, Nucleonics, **1963**, 33-35

6. Acknowledgments