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Optimization of the Processing of Mo Disks

Nuclear Engineering Division

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by
Peter Tkac, David A. Rotsch, Dominique Stepinski, Vakhtang Makarashvili, and George F. Vandegrift
Nuclear Engineering Division, Argonne National Laboratory

James Harvey,
NorthStar Medical Technologies, LLC

prepared for
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Office of Defense Nuclear Nonproliferation

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Peter Tkac, David A. Rotsch, Dominique Stepinski, Vakhtang Makarashvili,
James Harvey,* and George F. Vandegrift

Nuclear Engineering Division, Argonne National Laboratory
*NorthStar Medical Technologies, LLC

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ABSTRACT

The objective of this work is to decrease the processing time for irradiated disks of enriched Mo for the production of ^{99}Mo. Results are given for the dissolution of nonirradiated Mo disks, optimization of the process for large-scale dissolution of sintered disks, optimization of the removal of the main side products (Zr and Nb) from dissolved targets, and dissolution of irradiated Mo disks.

1 INTRODUCTION

Argonne National Laboratory (Argonne), in cooperation with Los Alamos National Laboratory (LANL), Oak Ridge National Laboratory (ORNL), and NorthStar Medical Technologies, LLC (NorthStar), is developing technology for the production of ^{99}Mo. As a short-term solution, NorthStar is planning to produce ^{99}Mo via ^{98}Mo(n, γ)^{99}Mo reaction at the University of Missouri Research Reactor (MURR). As a long-term solution, NorthStar will produce ^{99}Mo via the photonuclear reaction ^{100}Mo(γ, n)^{99}Mo from the irradiation of an enriched molybdenum target by an electron accelerator. A several-hundred-gram target is required to produce ~1000 Ci ^{99}Mo. Because ~1% of Mo-99 is lost per hour (due to decay), fast dissolution kinetics are required during processing.

Argonne's program to decrease the processing time for irradiated enriched Mo disks is multifaceted. We are both looking at means to decrease processing time by optimizing the dissolution process and equipment and, in collaboration with ORNL and NorthStar, are working to optimize the production of Mo sintered disks for high theoretical packing density and fast dissolution kinetics [1-3]. Here we report experimental results on:

i) dissolution of Mo disks to optimize production of Mo targets
ii) optimization of large-scale dissolution of sintered Mo disks
iii) optimization of removal of the main side reaction products, Zr and Nb, from dissolved targets
iv) dissolution of irradiated Mo disks (focus on radiochemical purity)

2 DISSOLUTION OF MO DISKS TO OPTIMIZE PRODUCTION OF MO TARGETS

2.1 INTRODUCTION

Previous dissolution studies [1-3] revealed several important features for the manufacturing of sintered Mo disks. First, high sintering temperatures, in general, lead to higher theoretical density of the disks, but decrease the dissolution rates. Second, high open porosity (a few per cent) is very important for good dissolution kinetics. In a few cases, however, disks with high packing density and low open porosity dissolved quickly (0.6 g/min), which could be related to the Mo particle size. Third, spray-dried sintered Mo disks showed very high dissolution rates in peroxide when pre-heated to 70°C (~2-3 g/min), but some disks dissolved too vigorously and would not be suitable for processing within a hot cell facility.

3-D printing is an option being considered for the production of targets. The use of thicker targets is also being considered, and therefore, understanding of thick target dissolution properties is required.

2.2 EXPERIMENTAL

Sintered Mo disks with different thicknesses (Figure 1) were fabricated by ORNL employing the spray-dried powder technique, followed by pressing at 138 ksi and sintering at 1600°C for 4 hours. These disks were dissolved in 50% hydrogen peroxide (Aqua Solutions, Inc., Technical grade, #H30504L) at room temperature (25°C). Some disks were heated to 70°C in a 2-L reaction kettle. Disk characteristics, dissolution times, and dissolution rates are summarized in Table 1.

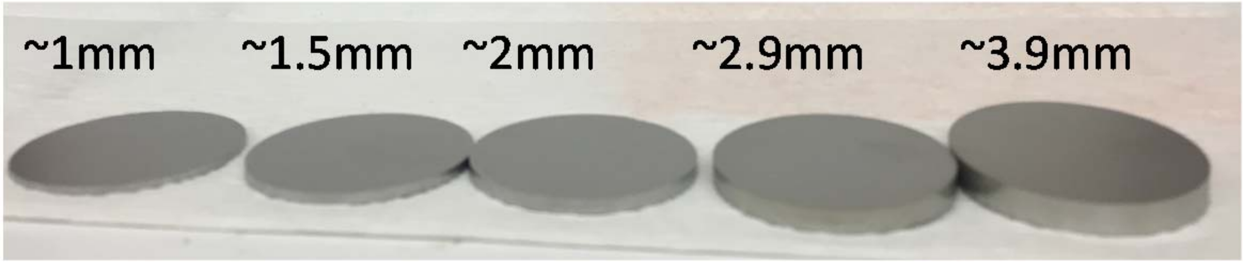

FIGURE 1 Photograph of spray-dried sintered Mo disks with different thicknesses from ORNL

2.3 RESULTS

The dissolution in the room temperature peroxide was very mild at the beginning. Very small bubbles started to form in the solution, and we observed no yellow color that would indicate dissolution of Mo (Mo-peroxo species form yellow species). Very little coloration was observed even after several minutes. When the disks started to dissolve (after several minutes, see Table 1), the reaction was very vigorous, with significant bubble formation (in some cases ~75-90% of the total volume of the vessel). Since the dissolution in room temperature peroxide was very slow, a 26 x 1 mm disk provided by NorthStar was also dissolved under the same conditions. This disk started to dissolve in ~15 sec, and completely dissolved in ~4.5 min with much less bubble formation during the dissolution. This finding clearly indicated a far different behavior compared with the ORNL disks.

Based on the slow dissolution in 50% H_2O_2 at room temperature, subsequent dissolution tests were performed in 50% H_2O_2 pre-heated to 70°C. It should be noted that a 2-mm disk (S100-26) dissolved extremely vigorously. Initially, 100 mL of 50% H_2O_2 at 70°C was added to a 2-L reaction kettle. Bubble formation was so vigorous that water was added to dilute and cool the solution and prevent the froth from escaping the dissolution vessel (bubbles filled the entire 2 L vessel expanding the initial volume of solution by 20x). For disks with larger masses (2.9-mm and 3.8-mm disks), peroxide was drained after spending 150 mL, and a fresh portion of 100 mL of peroxide was added. If more peroxide was needed, solution was drained again after another 150 mL of spent peroxide.

2.4 DISCUSSION

Differences in behavior during the dissolution studies of ORNL and NorthStar disks with no pre-heated peroxide could be attributed to the different morphologies of the disks. ORNL disks are produced from spray-dried powder that is composed of 50-150 µm large agglomerates formed from ~5 µm Mo powder particles, while NorthStar disks are most likely made from particles of only few micrometers (based on scanning electron microscopy images reported previously) [1].

There is no obvious trend indicating the effect of disk thickness on dissolution rates. One of the biggest concerns is the amount of bubbles forming during the dissolution, which could complicate the dissolution of larger quantities of disks (300-600 g). Another concern is that spray-dried sintered disks require a relatively long activation period (until they start dissolving) when room temperature peroxide is used, which leads to increased processing times and will require the use of a heating source during the dissolution.

TABLE 1 Summary of dissolution results for sintered Mo disks with different thicknesses

#	Disk Dimensions, mm	Mass, g	Origin	TD,[a] %	OP,[b] %	H_2O_2, °C	50% H_2O_2, mL	Diss. Time, min	Diss. Rate, g/min
S50-31	29.4×0.98	6.15	ORNL	90.8	3.1	25	80	16(8)[c]	0.38
S50-32	29.4×0.99	6.17	ORNL	90.6	2.8	70	100	4.5	1.37
S50-33	29.4×0.98	6.14	ORNL	90.6	2.9	70	100	3.75	1.64

TABLE 1 (Cont.)

#	Disk Dimensions, mm	Mass, g	Origin	TD,[a] %	OP,[b] %	H_2O_2, °C	50% H_2O_2, mL	Diss. Time,[c] min	Diss. Rate, g/min
S100-21	29.4×1.46	9.03	ORNL	89.8	5.5	70	150	3.25	2.78
S100-22	29.4×1.45	9.03	ORNL	89.7	5.5	25	100	18.25(15)	0.50
S100-23	29.4×1.48	9.04	ORNL	89.8	5.6	70	100	3.45	2.62
S100-26	29.4×1.94	12.03	ORNL	89.4	5.6	70	200	4	3.01
S100-27	29.4×1.94	12	ORNL	89.4	5.8	35	150	13.5(5.25)	0.89
S100-28	29.5×1.94	12	ORNL	89.1	6.1	70	200	13	0.92
S100-37	29.5×2.91	18.02	ORNL	89.7	5.1	70	450	27	0.67
S100-38[d]	29.5×2.9	18	ORNL	89.7	5.1	25	250	29.5(12)	0.61
S100-39[d]	29.5×2.9	17.92	ORNL	89.7	5.1	70	250	16.5	1.09
S100-43[d]	29.5×3.85	24.01	ORNL	89.1	5.4	70	450	24	1.00
S100-44[d]	29.6×3.83	23.82	ORNL	89	5.5	25	300	35.75(13)	0.67
S100-45[d]	29.6×3.84	23.88	ORNL	89	5.5	70	400	25	0.96
N/A	26×1	4.68	NorthStar	N/A	N/A	25	80	4.5(0.25)	1.04

[a] TD = theoretical density.

[b] OP = open porosity.

[c] Numbers in parentheses indicate when the disk started to dissolve vigorously, e.g., 18.25(15) – started to dissolve after 15 min, with dissolution completed in 18.25 min.

[d] After adding 150 mL, spent H_2O_2 was drained, and a fresh portion of 100 mL of 50% H_2O_2 was added.

2.5 CONCLUSION

Spray-dried sintered Mo disks require an activation period before the dissolution starts if non-heated peroxide is used. This is most likely due to the morphology of the disks, since they are composed of 50-150 µm Mo spheres formed from ~5-µm Mo powder particles. If pre-heated peroxide is used, high dissolution rates are observed, usually in the range of 0.6-3 g/min, which is the expected rate based on our previous studies.

3 OPTIMIZATION OF LARGE-SCALE DISSOLUTION OF SINTERED MO DISKS

3.1 INTRODUCTION

Processing of the irradiated Mo disks (310 g per batch), now being used at MURR, includes dissolution of the disks in hydrogen peroxide followed by partial evaporation of the solution, addition of ferric ion to form a precipitate to carry down impurities from the Mo solution, and conversion to a 5 M KOH solution. Currently, the time for performing this process at MURR is 5-6 hr, which is longer than desired for efficient production. Therefore, Argonne sought to find a method to minimize the total processing time.

3.2 EXPERIMENTAL

Dissolution experiments of up to 300 g of sintered Mo disks (provided by NorthStar and ORNL) were performed in 30% and 50% hydrogen peroxide in a glass reaction vessel. The 30% peroxide was un-stabilized (Fisher Chemical, #H325-4), and the 50% peroxide was stabilized with Sn (Aqua Solutions, Inc., Technical grade, #H30504L, or Sigma-Aldrich #516813) or phosphate (Acros Organics, #AC30286-0025). Natural Mo disks were dissolved in the peroxide and repeatedly drained into an evaporation/concentration vessel. After complete dissolution, the dissolved Mo was heated to destroy peroxide and to bring the solution to the desired volume. Then, KOH was added to make K_2MoO_4, 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 min. After filtration, KOH was added to make ~0.2 g-Mo/mL as K_2MoO_4 in 5M KOH solution. A Julabo F26 ED (0.26-kW cooling capacity at 20°C and flow rate of 15 L/min) chilling unit was used as a source for cold water for the condensers.

3.2.1 75-g Experiments

Two ~75 g batches of sintered Mo disks (NorthStar) were dissolved in a 2-L reaction kettle (Figure 2) using 50% H_2O_2, and one ~75 g batch (ORNL) was dissolved in 30% H_2O_2.

All three batches dissolved in ~30 min, independent of the hydrogen-peroxide concentration or source of the Mo disks. No additional heating was provided. Dissolution was performed by the addition of H_2O_2 aliquots to a vessel containing 75 g of Mo disks, and all vapors were exhausted into the ventilation system. As the dissolution started, the solution turned yellow and then orange. The orange-colored solution was transferred into an evaporation/concentration vessel, and a fresh portion of H_2O_2 was added to continue the dissolution. After complete dissolution, the remaining H_2O_2 was destroyed by heating, and KOH was added to make a K_2MoO_4 solution, which was later filtered.

FIGURE 2 2-L vessel used for dissolution of 75 g Mo disks. Vapor released during dissolution was exhausted into ventilation.

Although the dissolution times for all three batches were similar, total processing times for disks dissolved in 50% H_2O_2 were ~2 hr and 1 hr 40 min, respectively, while the total processing time for disks dissolved in 30% H_2O_2 was ~4 hr. When 30% H_2O_2 was used, larger volumes of peroxide were needed, and therefore, the evaporation/concentration step was significantly longer due to the larger volume of water.

3.2.2 300-g Experiments

For processing of 300 g Mo disks, the dissolution was performed in a 5-L reaction kettle that had a small frit (Figure 3, left) and was drain fitted to the bottom. The frit and drain allowed removal of the dissolved portion of Mo into a concentration vessel under a vacuum. However, the small size of the frit led to its clogging by undissolved Mo-disk material and significantly hindered the dissolution/concentration process. The reaction vessel was modified by adding a larger frit (Figure 3, right). Condensers were also added to the top of the dissolution vessel to minimize vapor release to the atmosphere. The condensers were connected to a collection flask to trap the condensed vapors.

The large-scale dissolution tests are summarized in Table 2, and the setup is depicted on Figure 4. Disks were loaded into the vessel, and peroxide was added either from the top or bottom of the vessel by a peristaltic pump. When the color of the solution changed from yellow to orange, addition of fresh peroxide was stopped, and the solution of dissolved Mo was transferred by vacuum into an evaporation vessel from the bottom drain. After draining the spent solution, fresh peroxide was added to continue the dissolution, and this process was repeated until full dissolution was achieved.

After complete dissolution and partial destruction of peroxide in the evaporation vessel, we added a saturated solution of KOH to make the solution pH=13-14 (about half of the total KOH needed for making the 0.2 g-Mo/mL solution as K_2MoO_4 in 5 M KOH), preventing formation of a Mo-peroxo precipitate. Upon complete destruction of the Mo-peroxo species, the solution became colorless. However, due to the presence of Fe in the Mo disks (non-high-purity Mo disks), an orange-brown precipitate formed during this process. When evaporation was complete and the desired volume reached, the solution was allowed to cool and was passed through a Polycap 36 TC (0.6/45 µm) filter.

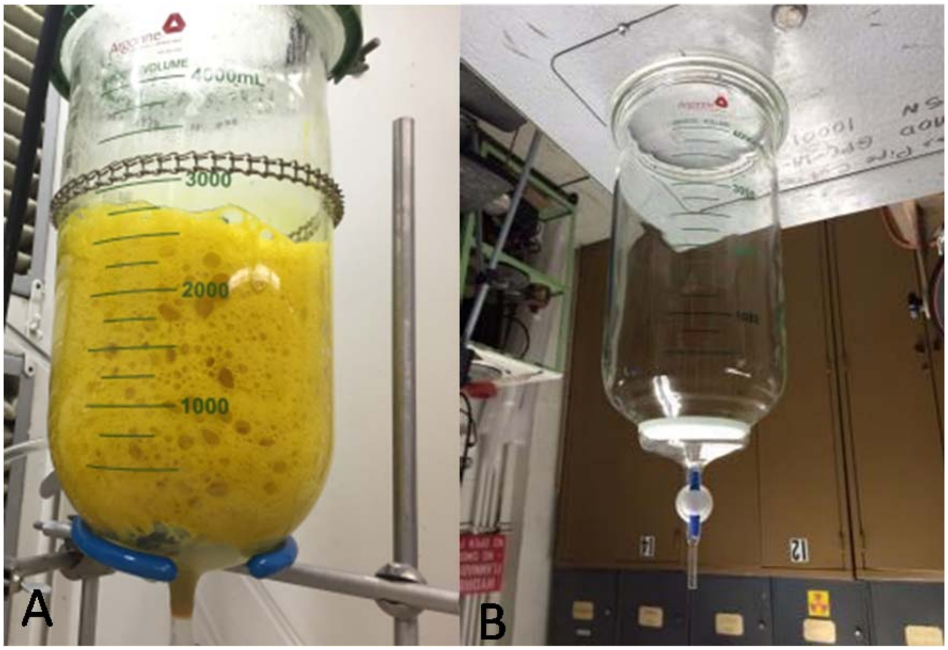

FIGURE 3 5-L vessels for dissolution of 300-g batches of sintered Mo disks. Vessels were designed with frit and drain valve on the bottom for easy removal of dissolved Mo in peroxide solution.

FIGURE 4 Setup used for dissolution of 300 g of sintered Mo disks

TABLE 2 Results of large-scale dissolution tests

#	H_2O_2, %	Diss. Vessel, L	Mo, g	Dissolution, hr	Evaporation, hr	Total, hr	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
8	50	5	300	1.5	0.6	2.3	vacuum
9	50	5	300	1.3	0.7	2.2	vacuum

As the large-scale dissolution experiments progressed, small changes to the setup were performed. For example, Figure 5 shows that when 50% peroxide was used, some of the dissolved Mo appeared in the collection flask (note yellow solution in collection flask). Also fixed glass adapters connecting condensers were replaced by flexible adapters to relieve the stress on the rigid glass components. This arrangement also lowered Mo losses by trapping some of the dissolved Mo in vapor in the adapters (Figure 6).

It should be noted that the chiller used did not provide sufficient cooling during the dissolution, and ice had to constantly be added into the chiller tank to keep the temperature below 5°C. The three condensers installed on the dissolution apparatus were not sufficient to collect all vapors from the reaction, and ~10% was estimated to have been exhausted to the atmosphere (semi-open condeners were used as shown in Figure 4). More efficient condensers were purchased and will be tested with a more efficient chiller (1.7-kW cooling capacity at 20°C and flow rate of 23 L/min). Dissolution studies using 600-g batches of sintered Mo disks are planned for the near future.

FIGURE 5 Presence of Mo-peroxo species in condensation flask (indicated by yellow color).

FIGURE 6 Flexible adapters used to connect condensers to dissolution vessel

Installation of a heating mantel and heat tape (Figure 7) helped to accelerate the evaporation process, and addition of a second condenser on the evaporation flask helped minimize pressure buildup and bubble formation during evaporation and addition of KOH. This change also minimized the time needed for the destruction of peroxide and the final concentration of the solution. However, in some rare cases, significant amounts of foam formed (especially when the vessel was under vacuum and if fresh peroxide was transferred to the evaporation flask). Therefore, a relief valve was installed on top of the evaporation flask (Figure 7) that, if opened, can relieve the negative pressure and lower the amount of foam/bubble formation.

The different times for dissolution and evaporation listed in Table 2 reflect these changes. A nearly finalized setup was used during dissolutions 7–9. As can be seen, the dissolution times for 50% and 30% H_2O_2 were very similar, 1.3–1.5 hr; however, the volume of peroxide added was significantly different. About 4.5 liters of 50% H_2O_2 was needed for complete dissolution, while for 30% H_2O_2 ~6.3 liters was spent. The latter led to a much larger volume that needed to be evaporated and, therefore, equated to a much longer processing time. Advantages of using 30% peroxide include minimal bubble formation during the dissolution process and easier decomposition and conversion of the solution into potassium molybdate due to less vigorous reaction. However, significantly shorter total processing times with 50% peroxide are very important for fast processing, which allows for faster generation of the Mo-99 product.

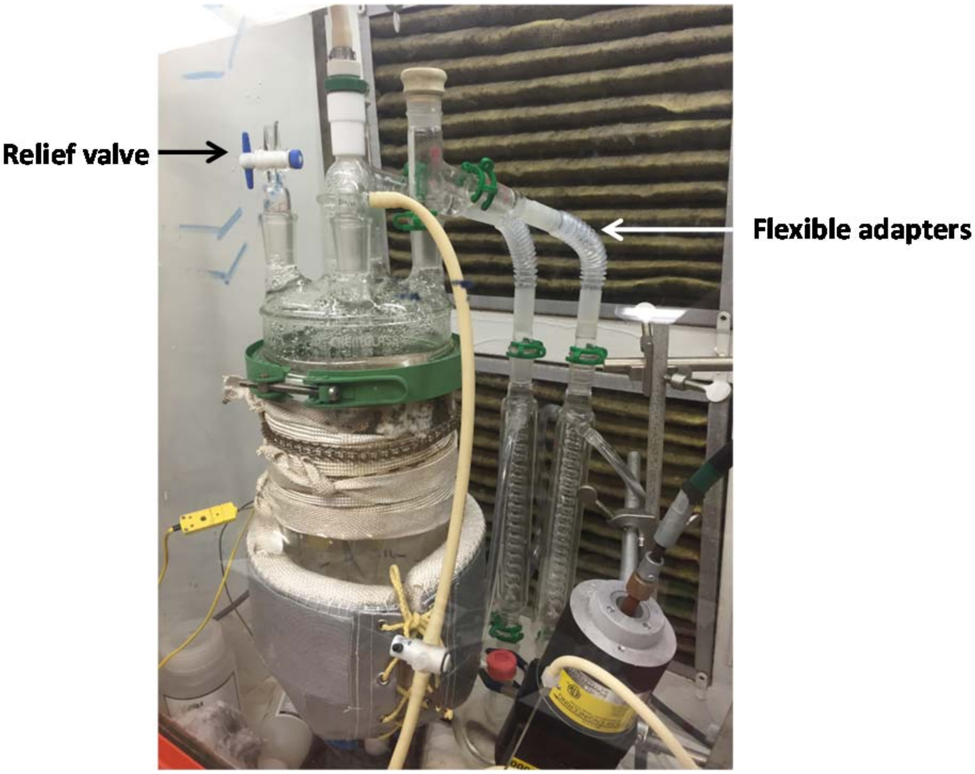

FIGURE 7 Evaporation vessel with heating mantel on the bottom and heat tape on top, which provides better heat distribution and accelerates the evaporation process.

3.3 CONCLUSION

Several large-scale dissolution tests were performed with up to 300 g of sintered Mo disks using 30 and 50% peroxide. The 75-g dissolution tests were performed in a 2-L kettle, while 300-g batches were processed in a 5-L kettle. Several modifications to the apparatus were made during these test trials. A series of condensers was installed to minimize the amount of water vapor exhausted during dissolution and to minimize the amount of bubbles formed during the peroxide destruction and concentration steps. Also, the addition of a heating mantel and insulation helped to significantly decrease the total processing time. These modifications lowered the processing time from ~8 hr to less than 2.5 hr. Further modification will be focused on providing sufficient cooling and optimizing the apparatus for use in a hot-cell facility.

4 REMOVAL OF ZR AND NB FROM DISSOLVED MO DISK SOLUTION

4.1 INTRODUCTION

During production of ^{99}Mo from irradiated Mo targets, several byproducts are generated, including Zr and Nb, which need to be removed during processing. According to NorthStar, MURR uses an Fe(III)-precipitation technique to remove Nb and Zr from the dissolved Mo solution; however, the precipitate is fine and hard to filter. Information provided by NorthStar is that MURR adds 10 mL of an iron nitrate solution that is 50 mg/mL Fe to about 1500 mL of Mo solution. In another study done by PG Research Foundation (Lisle, IL) for NorthStar, 4% vol% of ~1 M $Fe(NO_3)_3$ was added to the Mo solution, and good removal was achieved. Therefore, in our studies 0.7 vol% and 4 vol% of 1 M Fe solution were added to investigate the precipitation of Nb and Zr from Mo solutions.

In-situ formed magnetite has been used for removal of metal ions, including fission products and actinides, from solutions [4-11]. Magnetite is formed immediately by adding solution containing Fe(II) and Fe(III) ions to alkaline medium [4,5,8]. The magnetite particles remove metal ions from solution during the precipitation process. Several studies have indicated that pH has a major effect on co-precipitation of metal ions from solution [5,9,11]. Co-precipitation is very rapid, typically 5-10 min, and longer contact time does not increase the decontamination factors [5,10]. Co-precipitation was investigated using Fe(III), Fe(II)/F(III) in 1:1 ratio, Fe(II)/Fe(III) in 1:2 ratio, and commercial magnetite for removal of Pu, Np, and Sr. The 1:1 Fe(II)/Fe(III) showed better decontamination factors than Fe(III) alone or 1:2 Fe(II)/Fe(III), while decontamination factors with commercial magnetite were only in the single digits [4].

The chemistry of zirconium in water is best understood in terms of the complexation of Zr^{4+} with OH^-. The predominant aqueous complex species of Zr^{4+} over most of the pH range are of the type $Zr(OH)_y(H_2O)_{8-y}^{(4-y)}$, where y varies from 1 to 6 [12-14]. At pH >7 the predomint species have y = 5.

The molecular structures of niobates in aqueous solutions depend on the solution pH and metal oxide concentration. In alkaline solutions, niobium oxide contains different types of niobium-oxide ionic species, such as $H_xNb_6O_{19}^{(8-x)-}$ (x = 0-3) and $Nb_{12}O_{36}^{12-}$ polymers at higher concentrations. The presence of the different niobium-oxide ionic species is dependent on the solution pH. At high pH (~14.5), the hexaniobate ionic species $Nb_6O_{19}^{8-}$ exists in aqueous solutions. In the pH range 11.5–14.5, equilibria between the $Nb_6O_{19}^{8-}$ and $H_xNb_6O_{19}^{(8-x)-}$ (x = 1-3) hexaniobate ionic species exist in aqueous solutions [15–17].

This section discusses experimental work conducted at Argonne to study optimal conditions for removal of Nb and Zr from dissolved Mo solution. Methods investigated include co-precipitation with $Fe(NO_3)_3$ as well as 1:1 $Fe(NO_3)_3/Fe(SO_4)$ and $LaNO_3$, and adsorption by hydrous zirconium oxide (HZO) and commercial magnetite.

4.2 EXPERIMENTAL

Initial experiments utilized 0.1 M KNO_3 solution containing ~200 g/L Mo, which was prepared from MoO_3 (STREM Chemicals) and 45% KOH (Fisher) and KNO_3 (Sigma-Aldrich) and is referred to as Solution A. The pH of the solutions was brought to ~ 8.0, 12.4, 13.2, and 14.4, and the OH^- concentration to 5 M. The solutions were subsequently filtered with a 0.22-µm polyvinyl difluoride (PVDF) syringe filter. The composition of the solutions was confirmed by inductively coupled plasma mass spectrometry (ICP-MS), as given in Table 3. After preparation, the solutions were spiked with Zr-95/Nb-95 tracer.

TABLE 3 Composition of solutions prepared from MoO_3—Solutions A.

MoO_3 in KOH, Filtered			
pH	K (M)	Mo (g/L)	Fe (g/L)
8	4.12	197	< 1.44E-02*
12.4	4.17	197	< 1.44E-02*
13.2	4.37	208	< 1.44E-02*
14.4	5.17	197	< 1.44E-02*
5 M OH^-	9.21	204	< 1.44E-02*

* Below detection limit

Further tests used Mo disks obtained from ORNL that were dissolved in 30% H_2O_2 (Fisher Scientific) (Solution B). After dissolution, the solution volume was reduced by evaporation, the pH was brought to 12.3 and 13.5, and the OH^- concentration to 0.90 M and 4.7 M using 45% KOH. The solutions were filtered with a 0.22-µm PVDF syringe filter. The 0.90 M and 4.7 M OH^- solutions were titrated with a 0.100 M and 1.00 M HNO_3 volumetric standard (Sigma-Aldrich), respectively, using phenolphthalein indicator (Sigma Aldrich). The compositions of the solutions were confirmed by ICP-MS (Table 4). After preparation, the solutions were spiked with Zr-95/Nb-95 tracer.

Subsequent experiments used Mo disks obtained from NorthStar that were dissolved in 30% H_2O_2 (Fisher Scientific) in the presence of Zr-95/Nb-95 (Solution C). The solution volume was reduced by evaporation, and 45% KOH was added to bring the solutions to pH = 12, 13, and 14, and $[OH^-] = 5$ M; HNO_3 was used to adjust the pH as needed. Solutions were titrated with 0.100 M or 1.00 M HNO_3 volumetric standard (Sigma-Aldrich), using phenolphthalein indicator. The compositions of the unfiltered solutions were determined by ICP-MS (Table 5).

Temperature dependence studies were performed by shaking solution C in a thermostated bath for 20 min and filtering using a 0.22-µm PVDF syringe filter.

TABLE 4 Composition of solution B prepared from high-purity Mo disks.

Mo Disks Dissolved in H_2O_2 and KOH and Filtered			
pH	K (M)	Mo (g/L)	Fe (g/L)
12	3.73	171	< 1.44E-02*
13	6.39	285	< 1.44E-02*
0.90 M OH^- (titrated)	4.65	171	< 1.44E-02*
4.70 M OH^- (titrated)	8.11	173	< 1.44E-02*

* Below detection limit

The Zr-95 (Eckert and Ziegler, Valencia, CA) was obtained as 10 µg Zr/mL in 0.5 M oxalate solution. The oxalate was destroyed by contacting the solution with 1 M H_2O_2/0.3 M HNO_3 and bringing it to dryness three times. The Zr-95 was then dissolved in 0.1 M NaOH. Typically, 2 µL was added per 1 mL of the Mo solution. The combined activity of Zr-95 and its daughter Nb-95 was measured using a Perkin Elmer 1480 Wizard 3" NaI Gamma Counter in the 686-846 keV window. Both $Fe(NO_3)_3 \bullet 9H_2O$ (Sigma Aldrich) and freshly prepared $FeSO_4 \bullet 7H_2O$ (Sigma Aldrich) solutions were dissolved in 18 Ω deionized water. Hydrous zirconium oxide was prepared as described before. Magnetite was obtained from Sigma Aldrich, and $La(NO_3)_3$ was obtained from Argonne stocks.

TABLE 5 Composition of unfiltered solution C prepared from Mo disks

Disks Dissolved in H_2O_2 in the Presence of Zr-95/Nb-95, Unfiltered			
pH	K (M)	Mo (g/L)	Fe (g/L)
12	6.98	338	0.22
0.04 M OH^-	7.29	353	0.27
0.26 M OH^-	7.44	347	0.26
3.90 M OH^-	8.64	249	0.15

4.3 RESULTS

Experiments were performed using Solution A to investigate the effects of different OH^- concentrations on co-precipitation of Zr-95/Nb-95 radiotracers with $Fe(NO_3)_3$. Results are given in Table 6. When performing blank experiments with 0.22 µm PVDF and polypropylene (PP) syringe filters, we observed that 99.9+% of Zr and Nb can be removed from solution at pH 12-13 by filtration. The removal at pH 12-13 is not increased by addition of Fe(III). At pH 14, the removal is ~94% and can be increased to 99% by addition of Fe(III). At pH 8, Zr and Nb removal is low and will,therefore, not be further investigated. Precipitation of Zr and Nb in the solution reflecting the conditions of the NorthStar process solution of 200 g/L Mo, 9.3 M K^+, and 5 M OH^- is 45-65%, which is too low to satisfy process requirements.

TABLE 6 Removal of Zr and Nb from solution A prepared from MoO_3 at pH 8, 12, 13, and 14, and 5 M OH^-

	% Removal of Zr-95 and Nb-95 from Solution A			
pH	0.22 µm PP Filter	0.22 µm PVDF Filter	1 M $Fe(NO_3)_3$, 0.7 vol%	1 M $Fe(NO_3)_3$, 4 vol%
8	<0.1	0.67	3.13	8.37
12	99.97	99.99	99.98	99.34
13	99.94	99.98	99.96	99.57
14	94.43	94.72	95.34	98.98
5 M OH^-	55.17	45.59	59.50	65.06

The effect of peroxide on precipitation of Zr and Nb from Solution A was investigated by adding 30% H_2O_2 (1 µL/mL) to the solution and stirring for 15 min. Table 7 gives the percent removal of Zr and Nb with the PP filter, Fe(III), Fe(II)/Fe(III), HZO, commercial magnetite, and $La(NO_3)_3$. The presence of peroxide significantly decreased precipitation of Zr and Nb and caused inefficient removal by filtration or co-precipitation by Fe(III). Co-precipitation with Fe(II)/Fe(III) increased the removal of Zr and Nb to 99.8% at pH 13 and 95.3% at pH 14. The HZO addition achieved good separation, 99.9%, only at pH 13. Magnetite addition did not reach satisfactory decontamination. Lanthanum achieved good separation, 95.4% at pH 12 and >99.9% at pH 13.

TABLE 7 Removal of Zr and Nb from solution prepared from MoO_3 at pH 8, 12, 13, 14, and 5 M OH^- in the presence of H_2O_2

	% Removal of Zr-95 and Nb-95 from Solution A in the Presence of H_2O_2					
pH	0.22 µm PP Filter	1 M $Fe(NO_3)_3$, 4% vol%,	1 M, 1:1 Fe(II)/Fe(III), 4% vol%	HZO, 10 mg/mL	Magnetite	10 mg/mL $La(NO_3)_3$, 10% vol.%
8	0.10	12.9	49.2	22.1	7.2	67.8
12	82.41	83.2	75.4	76.8	16.8	95.4
13	74.35	77.8	99.8	99.9	83.5	>99.9
14	19.64	37.2	95.3	45.7	3.0	77.6
5 M OH^-	7.61	37.6	62.1	15.6	2.0	55.2

Table 8 gives the percent removal of Zr and Nb from Mo disks dissolved in H_2O_2 (Solution B) with PVDF filter, 0.7 vol% and 4 vol% Fe(III), 0.7 vol% and 4 vol% Fe(II)/Fe(III), and HZO. Filtration achieved 99.9% removal at pH 12-13 and 99.3% at 0.90 M OH^-. Co-precipitation methods and adsorption with HZO did not show clear and significant increase in Zr and Nb removal. All Zr and Nb removal procedures tested for Mo solution containing 4.70 M OH^- achieved 72-84% removal.

TABLE 8 Removal of Zr and Nb from solution B prepared from Mo disks dissolved in H_2O_2 and KOH at pH 12 and 13, 0.90 M OH^-, and 4.70 M OH^-

	% Removal of Zr-95 and Nb-95 from Dissolved Disk (Solution B)					
pH	0.22 µm PVDF Filter	1 M $Fe(NO_3)_3$, 0.7 vol%	1 M $Fe(NO_3)_3$, 4 vol%	1 M, 1:1 Fe(II)/Fe(III), 0.7 vol%	1 M, 1:1 Fe(II)/Fe(III), 4 vol%	HZO, 10 mg/mL
12	99.9	99.0	98.9	99.5	99.7	99.9
13	99.9	99.9	99.1	>99.9	99.7	>99.9
0.90 M OH^-	99.3	99.2	99.6	99.3	99.6	99.5
4.70 M OH^-	72.5	73.0	76.8	73.3	73.7	84.4

To further test the removal of Zr and Nb in the presence of peroxide, Mo disks were dissolved in H_2O_2 in the presence of Zr-95/Nb-95 radiotracer (Solution C), and the pH was brought to 12 and the OH^- concentrations to 0.04, 0.26, and 3.90 M with KOH (Table 9). Filtration with 0.22 µm PVDF filter removed 99.4-99.6 of Zr and Nb for 0.04-0.26 M OH^-. Co-precipitation with Fe(III) and Fe(II)/Fe(III) and adsorption by HZO did not significantly increase the removal. These results differ significantly from the results obtained for Zr and Nb removal from solutions prepared from MoO_3 (Solution A) and spiked with H_2O_2. Removal of Zr and Nb is much higher for solutions prepared by dissolving Mo disks in H_2O_2 in the presence of Zr/Nb radiotracer. The reason for this difference could stem from the presence of a large amount of Fe in the disks obtained from NorthStar. The presence of Fe could lead to precipitation of Zr and Nb during the dissolution and increase the removal of Zr and Nb.

TABLE 9 Removal of Zr and Nb from solutions prepared from Mo disks dissolved in H_2O_2 in the presence of Zr-95/Nb-95 radiotracer at pH 12 and 0.04, 0.90, and 4.70 M OH^---Solution C

	% Removal of Zr-95 and Nb-95 from Mo Disks Dissolved in the Presence of Zr and Nb (Solution C)			
pH	0.22 µm PVDF Filter	1 M $Fe(NO_3)_3$, 0.7 vol%	1 M, 1:1 Fe(II)/Fe(III), 0.7 vol%	HZO, 10 mg/mL
12	99.1	97.6	97.7	98.5
0.04 M	99.6	99.6	99.8	99.8
0.26 M	99.4	99.7	99.6	99.8
3.90 M	70.0	71.4	67.7	84.4

Solution C was also utilized to test the solubility of Zr and Nb precipitates at different temperatures (Table 10). In these experiments, solutions were shaken in a thermostated bath at 27.5, 40, 60, and 80°C for 20 min. Temperature did not have a significant effect on the solubility of the precipitates, and the Zr and Nb removal was not significantly affected at pH 12 and OH^- concentrations of 0.04, 0.26, and 3.90 M. The Fe concentrations in Solution C treated with Fe(III) and filtration, Fe(II)/Fe(III) and filtration, and solutions mixed at 40, 60, and 80°C were measured by ICP-MS and were at or near the detection limit of 1.13×10^{-2} g/L Fe.

TABLE 10 Effect of temperature on the solubility of Zr and Nb precipitates

	% Removal of Zr-95 and Nb-95 at Different Temperatures from Mo Disks Dissolved in the Presence of Zr and Nb (Solution C)			
pH	27.5°C, 0.22 µm PVDF Filter	40°C, 0.22 µm PVDF Filter	60°C, 0.22 µm PVDF Filter	80°C, 0.22 µm PVDF Filter
12	99.1	97.6	97.7	98.5
0.04 M	99.6	99.6	99.8	99.8
0.26 M	99.4	99.7	99.6	99.8
3.90 M	70.0	71.4	67.7	84.4

4.4 CONCLUSION

Both Zr and Nb can be efficiently removed from Mo solutions at pH 12-14 using 0.22 µm PP or PVDF filter. The ability to remove Zr and Nb by filtration will need to be further verified with high-purity Mo disks. The exact upper OH^- concentration limit, where Zr/Nb removal levels are acceptable, will need to be further verified. Also, a method for dissolution of Mo disks while achieving acceptable OH^- concentration in a hot cell setting will need to be developed. The presence of peroxide can decrease the precipitation and Zr/Nb removal levels. The effect of peroxide solution on speciation and precipitation of Zr and Nb will be further investigated by examining the potential role of stabilizers present in the peroxide solution on the speciation of Zr and Nb.

5 DISSOLUTION OF IRRADIATED MO DISKS: FOCUS ON RADIOCHEMICAL PURITY

5.1 INTRODUCTION

Four production runs were performed with six Mo-100 enriched targets. The Mo solution obtained from the first irradiation was loaded into a TechneGen generator (an older model of RadioGenix™) and processed at Argonne. Lower than expected and inconsistent Tc-99m yield results were observed. Solutions from the next three irradiations were sent to NorthStar for processing with the RadioGenix™ generator. These tests had low yield and very inconsistent results. The ABEC resin did not perform as desired, and this problem was thought to be the result of stabilizers found in the hydrogen peroxide solutions used to dissolve irradiated Mo-100 disks. To test this hypothesis, we irradiated four disks and dissolved three in peroxide solutions of 30% H_2O_2 (no stabilizer), 50% H_2O_2 with Sn as stabilizer, and 50% H_2O_2 with phosphate as stabilizer. After dissolution, 2 mole-equivalents of KOH was added per mole of Mo to make K_2MoO_4. The solutions were filtered through a 0.3-um filter, and more KOH was added to make the solution within the desired specifications (0.2 g-Mo/mL as K_2MoO_4 in 5 M KOH). Figure 8 shows a photograph of the final solution after dissolution and the 5 M KOH adjustment.

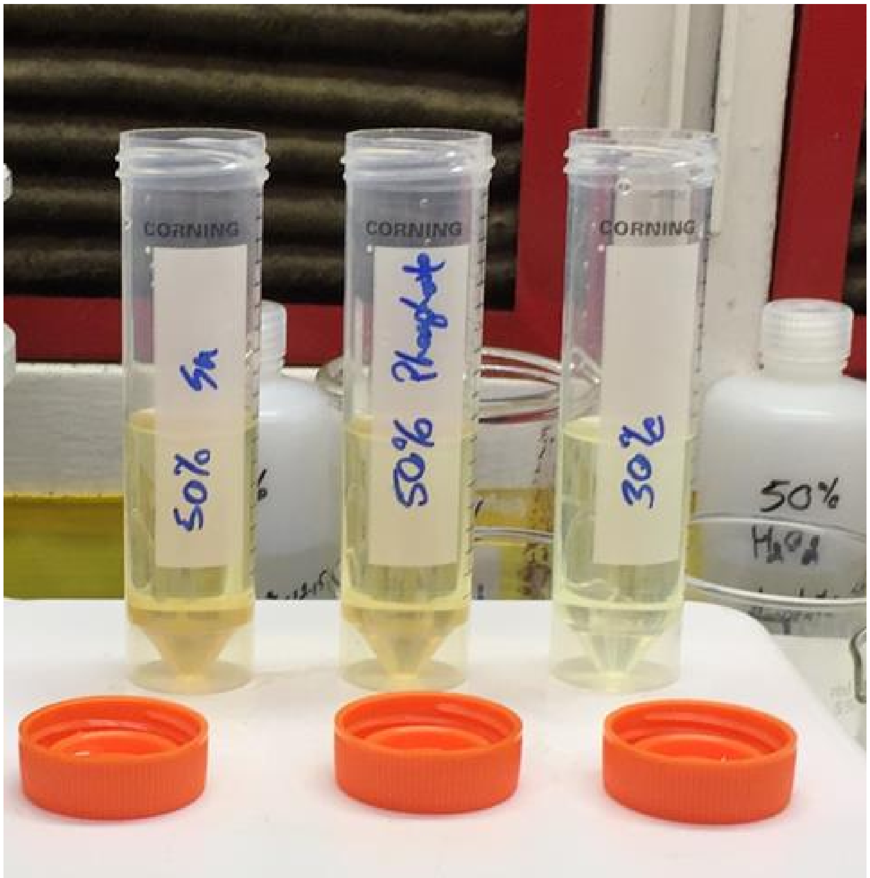

FIGURE 8 Photograph of solutions after dissolution of irradiated Mo disks in three H_2O_2 solutions: non-stabilized 30% H_2O_2 (right), 50% H_2O_2 stabilized with Sn (left), and 50% H_2O_2 stabilized with phosphate (middle)

Activities of Mo-99, Zr-95, Nb-95, and Nb-96 detected in the final solution (~24 mL) after filtration are listed in Table 11.

TABLE 11 Activities in three solutions obtained after dissolution of irradiated natural Mo disks

	μCi		
	Disk #1	Disk #2	Disk #3
Mo-99	692	507	612
Zr-95	1.40	1.65	1.07
Nb-95	3.74	5.21	2.07
Nb-96	4.85	5.94	1.95

5.2 SEPARATION OF TC AND MO USING POLYETHYLENE GLYCOL

Aqueous biphasic extraction chromatography (ABEC) resin utilizes stationary polyethylene glycol (PEG) to separate technetium and molybdenum. The ABEC resin is being used by NorthStar in their RadioGenix™ generator system to selectively sorb pertechnetate ion, while molybdate passes through the ABEC column. Technetium is then stripped from the column using normal saline solution.

In this effort, PEG-2000 was dissolved to obtain a 40 wt% aqueous solution (PEG stock solution). Partitioning studies were performed by contacting 0.5 mL of each solution (PEG stock solution and dissolved Mo-99 solution). The mixture was stirred vigorously for 2 min, followed by centrifugation for 2 min; this process was repeated once more. The phases were aliquoted for counting. Distribution coefficients (D values) and separation factors from a single experiment are shown in Table 12. Very little difference in the distribution coefficients was observed for the three H_2O_2 solutions.

TABLE 12 Distribution ratios and separation factors for Mo and Tc for PEG

	$D_{Tc\text{-}99m}$	$D_{Mo\text{-}99}$	Sep. Factor
30% H_2O_2	10.7	0.33	32.3
50% H_2O_2 (phosphate)	7.52	0.49	15.1
50% H_2O_2 (Sn)	9.96	0.12	83.3

The distribution coefficients for Mo-99 are consistent with literature values [18]. The Tc-99m coefficients are ten times lower than literature values and may be accounted for by the inherent differences in the manner in which the experiments were performed. The literature used a very dilute amount of Tc-99m and Mo-99 (a small spike) while our method used macro-quantities of Mo. This difference may have had an impact on the performance of the PEG solution.

5.3 CHROMATOGRAPHY EXPERIMENTS

Thin layer chromatography (TLC) is standard method for determining the radiochemical purity of Tc product. It is very simple method that can quickly identify the radiochemical purity of Tc product due to very different retention factors for pertechnetate [Tc(VII)) and Tc(IV)]. In this study, TLC was performed using filter paper strips with 80% acetone/20% 2M HCl as a mobile phase. Two 10-µL aliquots of Mo solution (0.2 g-Mo/mL as K_2MoO_4 in 5M KOH) were added to the paper, which was allowed to dry and developed in an acetone/2M HCl solution. Next, the strips were then cut into 11 fractions and gamma counted.

Due to the small activity loaded on TLC, 30-min gamma counting was performed. All data were decay-corrected. First, Mo was decay corrected to the start time of the count:

$$A_{Mo(0)} = \frac{A}{e^{-\lambda_{Mo} t}} \qquad \text{(Eq. 1)}$$

where $A_{Mo(0)}$ is the activity of Mo-99 at the start of the count, t is the length of time of the count, and λ_{Mo} is the decay constant for Mo-99

The Tc grow-in during the counting time was determined with the following equation:

$$A_{Tc} = 0.875 \frac{\lambda_{Tc}}{\lambda_{Tc} - \lambda_{Mo}} A(Mo)_0 (e^{-\lambda_{Mo} t} - e^{-\lambda_{Tc} t}) \qquad \text{(Eq. 2)}$$

This activity was subtracted from the Tc activity at the start of the counting process. The activity of Tc was then decay-corrected to the beginning of counting of each chromatogram similarly as for Mo, using Eq. 1 for Tc.

Although the TLC data (Figures 9–11) did not show evidence for Tc(IV) (TcO_2), which has retention factor R_f=0, the peaks for both Tc and Mo are very broad, and perhaps indicate that several species are present.

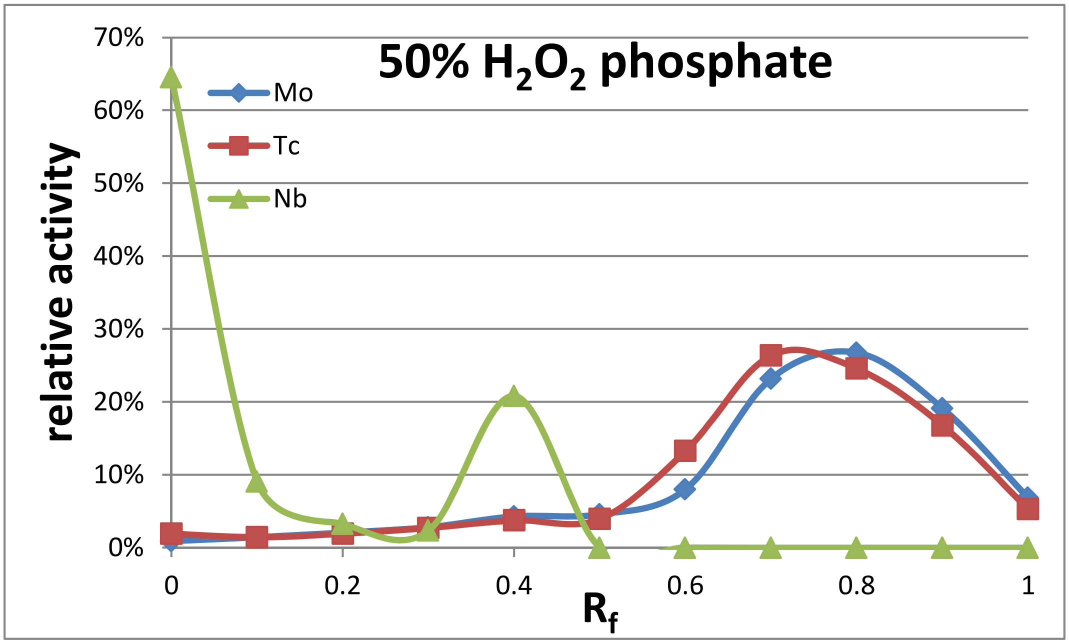

FIGURE 9 TLC data in 80% acetone/20% 2M HCl for Mo solution obtained after dissolution of Mo disk in 50% H_2O_2 stabilized with phosphate and filtration using 0.3-µm filter

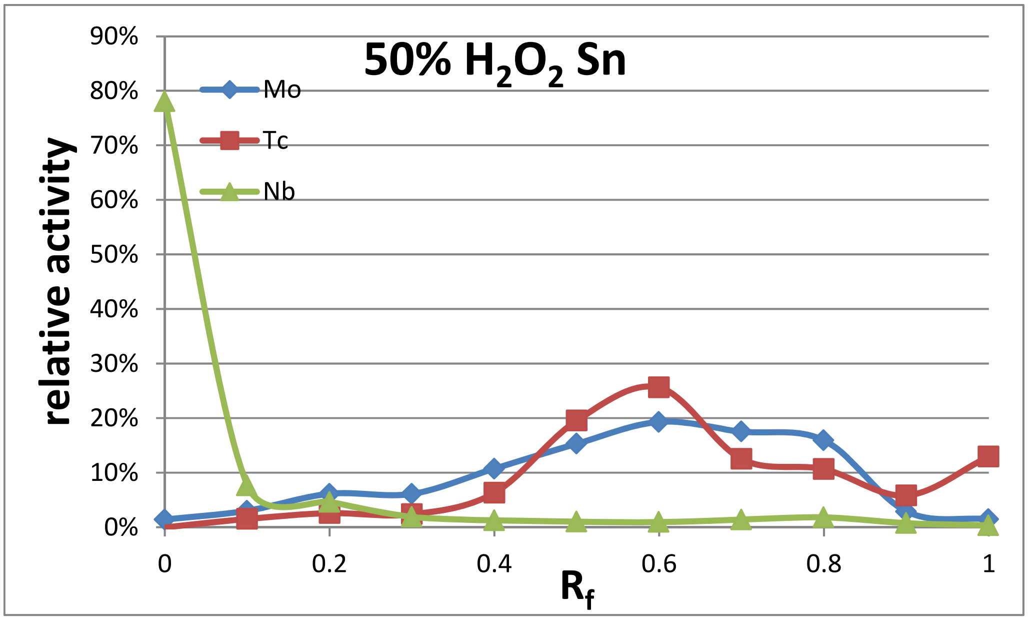

FIGURE 10 TLC data in 80% acetone/20% 2 M HCl for Mo solution obtained after dissolution of Mo disk in 50% H_2O_2 stabilized with Sn and filtration using 0.3-µm filter

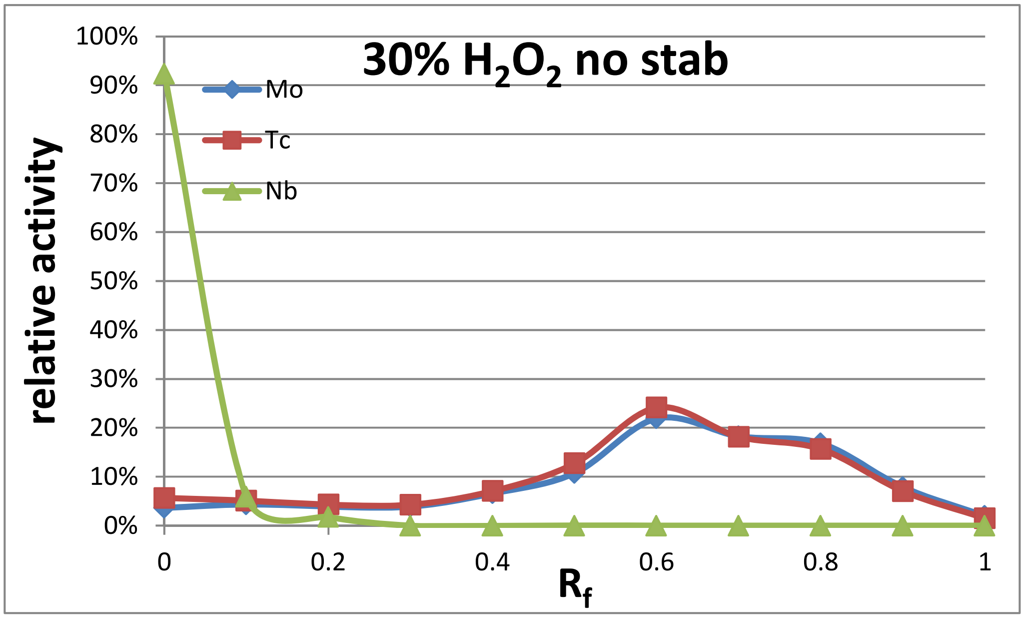

FIGURE 11 TLC data in 80% acetone/20% 2 M HCl for Mo solution obtained after dissolution of Mo disk in 30% H_2O_2 without any stabilizer and filtration using 0.3-µm filter

The good distribution ratios obtained by PEG extraction confirm that Tc is present as pertechnetate, since PEG is selective only for Tc(VII) (Table 12). The very broad peaks for Tc could be attributed to the formation of salt with larger cations, e.g., Tl, Ag, Cs [19], or other cations that could be present in natural Mo disks as impurities. This possibility will be investigated in the future. Several irradiations are planned with ultra-high purity Mo disks to eliminate impurity effects on the speciation of both Tc and Mo.

Broad peaks for Mo are most likely due to a change in the chemistry of Mo during the chromatography. Potassium molybdate present in dissolved solution converts to molybdenyl cation MoO_2^{2+} under acidic conditions (20% HCl in acetone used for TLC), which is most likely affecting the R_f values on TLC. However, Figures 9-11 show no reduction of Mo.

Interestingly, Nb shows some increased mobility in the sample obtained after dissolution in the phosphate-stabilized 50% H_2O_2, which could be due to some complexation between Nb and phosphate. This will be further investigated to determine if phosphate could cause a problem in the removal of Zr and Nb during filtration or co-precipitation by Fe.

5.4 CONCLUSION

Both PEG extraction data and TLC experiments show no evidence of the presence of reduced Tc(IV) (TcO_2). However, very broad peaks observed in the TLC could indicate the presence of several Tc species, which could be due to complexation of pertechnetate with larger cations that could be present in natural Mo disks as impurities. However, no significant effect of different peroxides used for dissolution was observed during the extraction studies using PEG. Niobium showed some increased mobility on TLC for the 50% peroxide samples stabilized with phosphate, which could be due to interaction with phosphate. Further experiments are planned.

6 REFERENCES

[1] P.Tkac, G. Vandegrift, and J. Harvey, *Dissolution of Sintered Mo Disks*, Argonne National Laboratory, Report ANL/CSE-13/19 (July 2012).

[2] 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).

[3] P. Tkac and G.F. Vandegrift, *Dissolution of Sintered Mo Disks*, Argonne National Laboratory, Report ANL/CSE-14/26 (September 2014).

[4] H.A. Arafat, S.B. Aase, A.J. Bakel, D.L. Bowers, A.V. Gelis, M.C. Regalbuto, J. Sedlet, and G.F. Vandegrift, *Parametric Studies on the Use of In Situ Formed Magnetite for the Removal of Sr and Actinides from Tank Waste at the Savannah River Site*, ANL/CMT/MAGNETITE-2002-02, http://www.ipd.anl.gov/anlpubs/2003/04/46360.pdf (2003).

[5] S.A. Slater, D.B. Chamberlain, S.A. Aase, B.D. Babcock, C. Conner, J. Sedlet, and G.F. Vandegrift, Sep. Sci. Technol., 32, 127–147 (1997).

[6] S.A. Slater, D.B. Chamberlain, C. Conner, J. Sedlet, B. Srinivasan, and G.F. Vandegrift, *Methods for Removing Transuranic Elements from Waste Solutions*, Argonne National Laboratory, Report ANL-93/43 (1994).

[7] T.E. Boyd, M.Y. Price, and R.L. Kochen, *Ferrite Treatment of Actinide Waste Solutions: Chemical Interferences in Actinide Removal by Ferrite Treatment*, Rocky Flats Plant, Report RPP-3601 (1985).

[8] T.E. Boyd and R.L. Kochen, *Ferrite Treatment of Actinide Waste Solutions: Continuous Processing of Rocky Flats Process Waste*, Rocky Flats Plant, Report RFP-3476 (1983).

[9] R.L. Kochen, *Actinide Removal from Aqueous Solution with Activated Magnetite*, Rocky Flats Plant, Report RFP-4100 (1987).

[10] T.E. Boyd, TR. L. Kochen, and M.Y. Price, "Removal of Radioactive Materials from Waste Solutions via Magnetic Ferrites," in *The Treatment and Handling of Radioactive Wastes*, Blasewitz, A.G., Davis, J.M., Smith, M.R., eds., Battelle Press, Columbus (1983).

[11] L.D. Banefield, J.F. Judkins, and B.L. Weand, *Process Chemistry for Water and Waste Water Treatment*, Prentice-Hall, Englewood Cliffs, NJ (1982).

[12] C.F.J. Baes and R.E. Mesmer, *The Hydrolysis of Cations*, John Wiley & Sons, New York (1976).

[13] D.W. Barnum, *Inorg. Chem.* **22**, 2297 (1983).

[14] J.H. Adair, R.P. Denkewicz, F.J. Arriagada, and K. Osseo-Asare, *Ceram. Trans.* **1**, 135 (1985).

[15] A. Goiffon B. and Spinner, *Bull. Soc. Chim. Fr*. 2435 (1975).

[16] A. Goiffon, R. Granger, C. Bockel, and B. Spinner, *Rev. Chim. Miner.* **10,** 487 (1973).

[17] J.M. Jehng and I.E. Wachs, J. Raman Spec. **22**, 83 (1991).

[18] R.D. Rogers, A.H. Bond, J. Zhang, and E.P. Horwitz, *Sep. Sci. Technol*. **32**(1–4) 867–882 (1997).

[19] E. Anders, *The Radiochemistry of Technetium*, National Academy of Sciences (1960).

Nuclear Engineering Division
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 208
Argonne, IL 60439-4854

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