

Optimization and Scale-up of Molybdenum-Recycle Process

Chemical Sciences and Engineering Division

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Optimization and Scale-up of Molybdenum-Recycle Process

by

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OPTIMIZATION AND SCALE-UP OF MOLYBDENUM-RECYCLE PROCESS

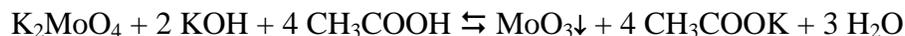
1 INTRODUCTION

Argonne National Laboratory (ANL), in cooperation with Oak Ridge National Laboratory (ORNL) and NorthStar Medical Technologies, LLC (NorthStar), is developing a recycling process for the solution containing valuable Mo-100 or Mo-98 enriched material from spent Mo-99/Tc-99m RadioGenix™ generators. The highly alkaline solution of K_2MoO_4 (0.2 g-Mo/mL in 5M KOH) from the spent RadioGenix™ generator contains about 1.8 kg of potassium per kilogram of molybdenum and recycling requirements for recovered Mo are 100 mg of K per kilogram of Mo (100 ppm). As part of the Mo recovery process, purification from several byproducts, such as Zr and Nb, is necessary. The final product of the full recycle process is conversion to Mo metal powder. Due to the high cost of enriched Mo material, the required Mo recovery yield is ~95%. In this report we focus on the processing of highly alkaline K_2MoO_4 solution in 5 M KOH, extraction of potassium, and conversion into MoO_3 powder. Based on previous experiments [Tkac 2013], we used acetic acid to precipitate Mo as MoO_3 . The produced MoO_3 powder is then sent to ORNL for further reduction to Mo metal and production of sintered Mo disks.

2 EXPERIMENTAL

2.1 PRECIPITATION OF MOLYBDENUM

Precipitation of Mo was performed by adding glacial acetic acid (AcA) to a solution of K_2MoO_4 in 5 M KOH (0.2 g-Mo/mL) with 5:1 volume ratio of acetic acid to K_2MoO_4 solution. The precipitation reaction is



The main advantage of using glacial AcA is that since it is a weak acid (equilibrium constant $K_a = 1.8 \times 10^{-5}$, where the pH of concentrated acid is ~ 1.8), the neutralization reaction is very mild. The Mo precipitate was then repeatedly washed with concentrated nitric acid. After precipitation of MoO_3 with AcA, washing with HNO_3 , and centrifugation, a fine white precipitate that contains Mo began to form. This product could be due to the presence of soluble dimeric or polymeric species and will be discussed in more detail later. To eliminate Mo losses, we allowed samples after the precipitation step with acetic acid and the first HNO_3 wash to sit for at least 24 hours.

After a final wash, the precipitate was re-dissolved and analyzed for K content using inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer SCIEX ELAN DRC II). For large-scale experiments, the MoO_3 precipitate after the final wash was dried at $160^\circ C$ and ground into powder. Then, an aliquot of MoO_3 was dissolved in NH_4OH , acidified to a final concentration of 5 M HCl, and submitted for ICP-MS analysis. Low potassium concentrations in the presence of high Mo concentrations can be determined after extracting Mo into 30% tributyl phosphate (TBP) from ~ 5 M HCl according to a procedure developed earlier [Tkac 2014a].

2.2 MIXING

For small-scale experiments using ~ 1 g of Mo, samples were mixed in a vortex mixer. Large-scale experiments with >40 g of Mo were performed with a Silverson L5M-A laboratory mixer at 7000 rpm.

2.3 CENTRIFUGATION

A Beckman centrifuge was used to separate the Mo precipitate from the acid. The samples were usually centrifuged at 3400 rcf (relative centrifugal force) for 5-10 minutes. For large-scale experiments that required 2 L bottles, we used a Thermo Scientific centrifuge (Sorvall RC 12BP+) at 6200 rcf.

3 RESULTS AND DISCUSSION

3.1 SMALL-SCALE EXPERIMENTS

Several experiments were performed when AcA was used to precipitate Mo from highly alkaline solutions and to wash the precipitate. Table 1 shows the results for the experiment with 60 mL of K_2MoO_4 in 5 M KOH (sample #103 and #104). About 300 mL of AcA was used to precipitate Mo and to perform two washing steps. Then, the Mo precipitate was washed 12 times with ~280 mL of 70% HNO_3 . We also performed small-scale experiment using 5 mL of K_2MoO_4 solution in 5 M KOH and addition of multiple elements (Li, Be, B, Na, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Nb, Ag, Cd, In, Sn, Sb, Cs, Ba, Hf, Ta, W, Re, Hg, Tl, Pb and Bi) (#105-106). After precipitation with 25 mL AcA, we performed two washing steps with 25 mL AcA and 12 washes with 25 mL HNO_3 ; samples were mixed for 2 minutes for each step and centrifuged. Potassium concentration was below 100 ppm for all samples, and good Mo yields were observed, 93-100%.

Table 2 shows the concentration of various elements in the starting solution and recovered Mo material for samples #105 and #106. The majority of elements were removed from the product, although the concentrations of Ti, V, As, Cd, Sb, and W were above 25 ppm.

To optimize the recovery process, we investigated the effectiveness of both AcA and HNO_3 for removal of potassium and Mo yield. Experimental data on the effectiveness of AcA and HNO_3 as washing agents are presented in Table 3. If acetic acid is used to precipitate Mo, about 80% of the potassium is removed with ~0.5% Mo losses. Although the precipitation reaction usually leads to formation of a Mo precipitate and a clear solution, over time a fine precipitate appears in the solution. This effect is most likely due to the formation of soluble polymeric Mo species that form at pH~4 [Cotton 1988]:

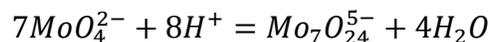


TABLE 1 Mo Yields and K Concentrations in the Recovered Mo Material. ICP-MS data reported with 10% uncertainty.

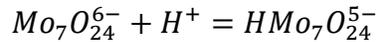
Sample No.	K_2MoO_4 in 5 M KOH, mL	Precipitation + 2 washes	HNO_3 Washes	K, ppm	Mo yield, %
103	60	300 mL AcA	12×280 mL HNO_3	42.0	103
104	60	300 mL AcA	12×280 mL HNO_3	39.7	94.9
105	5	25 mL AcA	12×25 mL HNO_3	74.0	92.6
106	5	25 mL AcA	12×25 mL HNO_3	59.6	94.8

TABLE 2 Concentrations of Various Elements in Starting Solutions and Recovered Mo Material. ICP-MS data reported with 10% uncertainty.

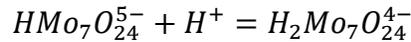
Content, ppm (mg of metal per kg-Mo)							
Element	Starting Solution	#105	#106	Element	Starting Solution	#105	#106
K	1,890,000	74	60	As	49.4	71.3	67.7
Li	38.0	ND	ND	Se	ND	ND	ND
Be	44.8	ND	ND	Rb	118	1.30	1.90
B	76.1	2.17	3.10	Sr	6.59	0.15	0.20
Na	642	17.0	23.7	Zr	36.1	0.44	0.31
Mg	28.5	12.5	19.9	Nb	27.1	17.0	20.8
Al	85.8	9.03	10.4	Ag	ND	ND	ND
Si	989	ND	ND	Cd	1660	1240	1290
P	ND	ND	ND	In	29.5	0.77	0.73
Ca	ND	ND	ND	Sn	54.7	2.30	1.67
Ti	54.1	32.2	32.1	Sb	53.4	28.8	24.2
V	58.0	81.6	91.0	Cs	54.3	4.53	4.89
Cr	25.7	ND	ND	Ba	3.64	3.70	3.96
Mn	1.77	0.37	0.77	Hf	43.3	0.42	0.33
Fe	ND	ND	ND	Ta	17.8	21.0	21.6
Co	1.20	ND	ND	W	165	153	152
Ni	ND	ND	ND	Re	49.5	0.51	0.84
Cu	59.7	2.49	11.4	Hg	7.10	2.88	2.98
Zn	83.5	ND	12.4	Tl	41.0	2.43	2.32
Ga	48.2	ND	ND	Pb	49.3	0.59	1.15
Ge	52.9	3.46	ND	Bi	28.0	0.42	0.14

ND – not detected.

Equilibria may then also be established for the following reaction:



and



Additional isopolyanionic forms of molybdenum may develop via the reaction:



These species probably decompose over time to hydrated MoO₃ and form the fine precipitate. Therefore, sufficient time is required for this conversion to keep the Mo recovery as high as possible.

TABLE 3 Experimental Data on the Effectiveness of AcA and HNO₃ for Removal of Potassium. Data are reported with 10% uncertainty.

Step	Volume, mL	Reagent	K removed, %	Mo, %	mg of K/kg of Mo
Precipitation	25	17.4 M AcA	80.0	0.47	
Wash #1	25	17.4 M AcA	8.8	0.10	
Wash #2	25	17.4 M AcA	2.3	0.18	
Wash #3	25	15.9 M HNO ₃	13.7	0.75	
Wash #4	25	15.9 M HNO ₃	3.3	0.35	
#111		Product*	1.05%	95.15%	20219
Precipitation	25	17.4 M AcA	78.1	0.48	
Wash #1	25	17.4 M AcA	7.4	0.11	
Wash #2	25	15.9 M HNO ₃	15.6	1.22	
Wash #3	25	15.9 M HNO ₃	3.9	0.58	
Wash #4	25	15.9 M HNO ₃	0.9	0.31	
#112		Product*	0.50%	96.86%	9403
Precipitation	25	17.4 M AcA	81.5	0.59	
Wash #1	25	15.9 M HNO ₃	23.4	1.25	
Wash #2	25	15.9 M HNO ₃	3.0	0.25	
Wash #3	25	15.9 M HNO ₃	0.6	0.19	
Wash #4	25	15.9 M HNO ₃	0.2	0.18	
#113		Product*	0.14%	96.48%	2703.1
Precipitation	25	15.9 M HNO ₃	84.9	5.44	
Wash #1	25	15.9 M HNO ₃	11.2	0.46	
Wash #2	25	15.9 M HNO ₃	1.4	0.25	
Wash #3	25	15.9 M HNO ₃	0.2	0.32	
Wash #4	25	15.9 M HNO ₃	0.04	0.40	
#114		Product*	0.017%	91.96%	347.3

*Percentages of K and Mo in final product.

When HNO₃ is used to precipitate Mo, the Mo losses in the first precipitation step are significantly higher than those when acetic acid is used (5.44% vs. about 0.5%). Results also clearly show that nitric acid is more proficient in removing potassium, and the sooner the AcA is replaced by HNO₃ to wash the Mo precipitate, the more effective is the removal of potassium. The formation of fine precipitate is most likely due to the presence of a soluble dimeric species, H₂Mo₂O₆²⁺ [Esbelin 2001], that temporarily forms through the protonation of molybdenum trioxide but then precipitates as Mo oxide [Tkac 2014b].

The data in Table 4 show the effectiveness of potassium removal when nitric acid washing is used after the precipitation of Mo with acetic acid. These small-scale experiments (Tables 3 and 4) showed that the best potassium removals and Mo recoveries are obtained when acetic acid is used to precipitate Mo, followed by washing the Mo precipitate with concentrated nitric acid. Additionally, prolonged mixing has a positive effect on removal of potassium in the final product, and better Mo purity can be achieved with the same number of washing steps. Molybdenum recoveries were in the range of 98-100%.

It was also demonstrated that when recycled MoO₃ material contains a high amount of potassium, further potassium removal can be accomplished by the reduction process. Recycled MoO₃ powder containing 190 mg-K/kg-Mo was sent to ORNL for reduction and then analyzed for potassium. The concentration in the reduced Mo powder was 40 mg-K/kg-Mo, indicating a decontamination factor of ~4.8.

We also investigated an option to recycle the nitric acid that is used in the washing steps to remove potassium from the Mo precipitate. Acetic acid that is used to precipitate Mo contains 60-70 g-K/L, and the first HNO₃ wash contains ~1.6 g-K/L, but if the first HNO₃ wash is disposed, the rest of the HNO₃ fractions contain 100-200 mg-K/L. Combined nitric acid washes containing ~165 ppm of potassium were distilled by rotary evaporation, and condensed (recycled) HNO₃ was submitted for ICP-MS analysis to determine the potassium concentration. The potassium concentration in the recycled HNO₃ was very low (~0.1 ppm), which could significantly reduce the volume of nitric acid waste. Recycled HNO₃ containing ~0.1 mg-K/L could be used in the first 4-5 HNO₃ washes.

3.2 LARGE-SCALE EXPERIMENTS

For large-scale experiments, a fresh solution of K₂MoO₄ in 5 M KOH was prepared and analyzed by ICP-MS to determine the starting Mo and K concentrations. Table 5 shows the concentrations of K and Mo in the starting solution and in the recovered Mo material. The

TABLE 4 Effect of the Number of Washes with HNO₃ and Mixing Time on Removal of Potassium from the Final MoO₃ Product. Mo was precipitated using AcA

Sample	Mixing time, min	No. HNO ₃ washes	Product Content		
			K Removed, %	Mo, %	mg of K/kg of Mo
#115	4	6	99.956	98.1	777.3
#116	4	8	99.985	99.5	261.2
#117	4	10	99.992	99.4	142.7
#118	4	12	99.996	96.7	71.6
#120	10	12	99.999	~100	14.7
#121	10	14	99.999	~100	10.8

TABLE 5 Mo and K Concentrations in the Starting Solution and Recovered Mo Material for Large-Scale Experiment^a

Sample #	Start Mo Solution, g	Mo, M	Total Start Mo, g	Total Start K, g	MoO ₃ Product, g	Mo Product, g	K Product, mg	Mo Yield, %	K, ppm
125	515	2.06	65.8	117.1	87.0	55.2	6.53	83.9	118.3
126	515	<u>KOH, M</u> 4.87	65.8	117.1	89.3	57.4	7.84	87.2	136.6
		<u>Mo, g/mL</u> 0.198							
Whole batch	1030		131.5	234.1	176.3	112.6	14.4	85.6	127.6

^a ICP-MS data reported with 10% uncertainty. K/Mo mole ratio: 4.37. A volume of 3.2 L of acetic acid was used to precipitate Mo, and 27 L of nitric acid was used in all washing steps.

ICP-MS results from the large-scale Mo recovery process showed that after nine washes with nitric acid, 99.994% of the potassium was removed, and its concentration in the final MoO₃ product was ~128 ppm.

Because of the difficulties with dispersing the Mo precipitate during the first and second nitric acid washes, the concentration of potassium in the final product was expected to be even higher, which indicates good mixing. The Mo recovery yield was ~86%. About 5% of the molybdenum was found in the acetic acid fraction, and the remaining portion was found in the nitric acid fraction.

Table 6 shows the data for the elemental concentrations in the starting solution and recovered MoO₃ product. Besides K, Si, and W, concentrations of all other elements in the final product were below 25 ppm. The starting solution had a high concentration of Si, which was most likely leached out from the glass volumetric flask during solution preparation. To avoid the introduction of Si into the starting solution, K₂MoO₄ should be prepared and stored in a non-glass container.

TABLE 6 Concentrations of Elements in the Starting Solution and Recovered Mo Material. ICP-MS data reported with 10% uncertainty.

	Content, ppm (mg of metal per kg-Mo)		
	Starting Solution	#125	#126
K	1,780,000	118	137
Si	1630	266	278
P	ND ^a	ND	ND
Cr	ND	10.5	14.7
Mn	2.97	1.24	1.13
Fe	ND	ND	ND
Ni	ND	3.35	1.86
Na	NA ^b	23.9	18.5
Mg	NA	0.72	16.3
Al	NA	0.80	0.88
Ti	NA	4.75	4.58
Co	NA	0.02	0.01
Cu	NA	3.66	0.91
Zn	NA	3.57	0.93
Sn	NA	0.11	0.10
W	NA	35.2	36.5

^a ND- not determined.

^b NA- not analyzed.

A portion of the recovered MoO_3 powder was converted into ammonium molybdate ($(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}$) by dissolving it in ammonium hydroxide. After air drying, both $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}$ and MoO_3 were sent to ORNL for reduction to Mo metal. The sample of MoO_3 (#126) was reduced to Mo metal, pressed into sintered Mo disks that were dissolved in hydrogen peroxide, and analyzed for potassium with ICP-MS. The concentration of potassium in recycled Mo material was 98 ppm (compared with 137 ppm of K in the recycled MoO_3 for sample #126, Table 6). This result might indicate some removal of potassium during the reduction process, but as previously discussed, it differs significantly from the results for a small-scale recovered powder that showed a decrease in potassium concentration from 190 ppm (recovered MoO_3) to 40 ppm (reduced Mo powder). As more samples of recycled MoO_3 material are reduced to Mo metal, we should be able to determine the decontamination factor for K during the reduction process more precisely.

We also processed ~4.5 L of K_2MoO_4 solution obtained after chemical processing of irradiated natural Mo targets in the University of Missouri Research Reactor. Molybdenum recovery yields were in the range of 93.4-95.8%, bringing the total amount of recovered MoO_3 powder to ~1.24 kg. Potassium concentrations in the final products were in the range of 41-213 ppm. Results are discussed in more detail in a separate report [Tkac 2014b].

4 SUMMARY

Small-scale experiments showed the most effective way of removing potassium from recovered MoO_3 product is to use acetic acid in the precipitation step, followed by multiple HNO_3 washes. It was demonstrated that the final concentration of potassium in the MoO_3 product can be affected by mixing time and the number of HNO_3 washes. Molybdenum recoveries near 100% were obtained for the small-scale experiments. Large-scale experiments showed good removal of potassium, although Mo recoveries were about 95% or less.

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