ANL-23/48

Recovery of Enriched Mo-100 from Low Specific Activity Mo-99/Tc-99m Generator Waste Streams

---

Chemical and Fuel Cycle Technologies Division

About Argonne National Laboratory
Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Lemont, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free at OSTI.GOV (http://www.osti.gov/), a service of the US Dept. of Energy's Office of Scientific and Technical Information.

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):

U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Road
Alexandria, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703) 605-6000
Fax: (703) 605-6900
Email: **orders@ntis.gov**

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: reports@osti.gov

Disclaimer
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

ANL-23/48

Recovery of Enriched Mo-100 from Low Specific Activity Mo-99/Tc-99m Generator Waste Streams

---

by
David J. Bettinardi, Timothy Lichtenstein, and Peter Tkac
Chemical and Fuel Cycle Technologies Division, Argonne National Laboratory

September 2023

CONTENTS

1. INTRODUCTION 1
    1.1 Solvent Extraction Approach 1
    1.2 Electrochemical Approach 2
2. EXPERIMENTAL 3
    2.1 Chemicals and Methods 3
        2.1.1 Solvent Extraction 3
        2.1.2 Electrochemistry 4
3. RESULTS 5
    3.1 Solvent Extraction 5
        3.1.1 Effect of NaOCl in Dilute and Concentrated Streams 5
        3.1.2 Decontamination from Na and K 6
        3.1.3 Effects of Strip Conditions on Mo Recovery and Phase Behavior 8
        3.1.4 Modified Processing Scheme 9
    3.2 Electrochemistry 10
        3.2.1 Electrochemical Characterization 11
        3.2.2 Electrolysis Tests and Characterization 11
4. CONCLUSIONS 15
5. AcKNOWLEDGEMENTS 15
6. REFERENCES 15

FIGURES

1 A picture of salt (possibly NaCl/NH_4Cl) precipitating in the organic phase and interface during stripping with concentrated NH_4OH. The aqueous phase was removed and is not shown 9

2 Top - the original MOEX scheme (adapted from reference 2). Bottom - the modified scheme for recycling of Mo from waste streams. 10

3 Cyclic voltammogram of a stainless-steel plate in the NaOH-KOH-Mo salt swept at 50 mV s^{-1} 11

4 A photograph (a) and a photomicrograph (b) with EDS mapping for the recovered cathode from constant potential electrolysis. 13

5 A photograph (a) and a photomicrograph (b) with EDS mapping for the recovered cathode from constant current electrolysis. 14

TABLES

1. Concentration ranges of the chemicals present in waste streams. 2
2. Simulant solutions A and B were prepared at two different chemical compositions. Metal constituents (Mo, Na, K) were verified by ICP-MS. Concentrations measured by ICP-MS are within ±10% of their reported values. 3
3. Results from the acidification of waste streams to 5M HCl, extraction into 30%-TBP/TCE, and stripping with 22% NH_4OH. Conditions tested included the addition of fresh bleach, the addition of no bleach, and waste stream dilution. 6
4. Elemental profiles of Mo, Na, and K in Simulant A during acidification, extraction (1×), scrub (1×), and stripping (1×). Concentrations measured by ICP-MS are within ±10% of their reported values. 7
5. Elemental profiles of Mo, Na, and K in Simulant B during acidification, extraction (1×), scrub (1×), and stripping (1×). Concentrations measured by ICP-MS are within ±10% of their reported values. 7
6. Mo extraction results after contact with varying strip phases from 8–22% NH4OH. The organic phase was extraction Mo (from 4 M HCl) in 30% TBP/TCE. 8

ABSTRACT

This study assessed two potential techniques for the extraction of pure Mo-100 target material from Mo-99/Tc-99m waste streams: 1) an established solvent-extraction method tailored for Mo-99 spent solution recycling, and 2) a low-temperature molten salt electrochemical process. By making minor modifications to the conventional solvent extraction method, particularly to accommodate the altered solubility limits arising from elevated Na+ concentrations in the waste, we achieved quantitative Mo recoveries. Although the electrochemical technique offers advantages in scalability and processing simplicity, it proved ineffective in recovering Mo from a NaOH-KOH salt melt.

1. INTRODUCTION

During the chemical processing of Mo-100 targets after irradiation, the Mo is dissolved in H_2O_2 and converted to K_2MoO_4 at a high pH [1][2]. The concentration of Mo solution used in low specific activity generators is 200g/L Mo in 5 M KOH. Once the expiration time of the generator source solution has elapsed, this decayed Mo-99 source is removed from the generator and sent back to the manufacturer for recycling, where a solvent extraction method is used to recover pure Mo from the generator source solutions [1].

During the operation of the generator, the waste stream collects saline elution washes, NaOH washes, and water washes along with a small fraction of the Mo material that must be recovered. The waste stream contains a blend of hydroxides (NaOH, KOH) and NaCl in an aqueous solution with Mo. Previously, the waste stream was solidified in a hydrogel copolymer consisting of crosslinked poly(acrylamide-co-acrylic acid). Recovery of Mo from the copolymer matrix involved an initial deswelling step with HCl, which collapses the hydrogel, releases Mo (>99%), and densifies the polymer into a solid waste form [3]. But partial dissolution of the organic polymer led to third-phase formation during solvent extraction. The copolymer was removed from later flowsheet designs to avoid adding complicated steps on the back end to fully recover Mo-100 from all streams.

Here, we tested both the solvent extraction recovery of Mo and the suitability of the NaOH-KOH eutectic for the electrolytic recovery of Mo.

1.1 SOLVENT EXTRACTION_APPROACH

The concentration ranges of the waste stream are provided in Table 1. Recovering Mo from this stream requires decontamination primarily from Na^+, K^+, Cl^-, and NO_3^-. This is theoretically achievable using the molybdenum extraction (MOEX) solvent extraction recycling process, which was established for the recycling of generator source solutions. The current implementation of MOEX in Mo recycling is as a 10-stage flowsheet, where MoO_2^{2+} is extracted into tri-*n*-butyl phosphate in tetrachloroethylene (TCE) from an HCl matrix. This process can be run on polyether ether ketone (PEEK) centrifugal contactors [4] and shows high decontamination factors for K$^+$ and Na$^+$. These flowsheet conditions must be laboratory-tested to evaluate solution characteristics and Mo recovery in the presence of high aqueous Na$^+$ concentrations, which is minimally present in generator source solutions.

Table 1. Concentration ranges of the chemicals present in waste streams.

Component	Concentration range (mol/L)
NaOH	1.9×100 – 2.3×100
Mo	2.3×10-2 – 1.9×10-1
NaCl	5.7×10-2 – 6.1×10-2
KOH	6.9×10-2 – 5.7×10-1
KNO3	1.6×10-3 – 1.3×10-2
NaOCl	3.1×10-6 – 2.6×10-5

1.2 ELECTROCHEMICAL APPROACH

Considering alternatives to solvent extraction is also worthwhile. Ion exchange columns, which offer a targeted and efficient means of selectively separating and concentrating specific ions (MoO_4^{2-}) from intricate waste streams, are less favorable in this scenario due to their limited loading capacities. For instance, employing alumina with a loading capacity of 20 mg Mo/g would require a substantial 40-kg column to meet the weekly processing requirement of 800 g-Mo. Given the high waste volume, salt content, and low Mo concentration, electrochemical processing from a salt melt could offer a more streamlined and potentially cost-effective recovery route.

Electrochemical reduction can be employed industrially to produce metals from either dissolved or solid compounds at high efficiencies. Molten salts have previously been used to produce Mo compounds from oxide species dissolved in the salt using electrochemical methods [5]. However, the molten salts used in those methods have high melting temperatures and are intolerant of any moisture impurities, meaning that the K_2MoO_4-hydroxide mixture would require thorough drying before being processed in those salts. Alternatively, molten hydroxide salts have low melting temperatures, have demonstrated solubility for oxide materials [6], and can be used to produce metal from dissolved oxide feedstocks by electrolysis [7]. During electrolysis in molten hydroxide salts, the cation of the oxide is reduced to metal and deposits at the cathode and the anionic oxygen species is discharged at the anode as gaseous oxygen. NaOH-KOH forms a low-melting-temperature eutectic that can solubilize oxide materials [5] and may be an appropriate electrolyte for recovering Mo from a processed target solution. Both NaOH and KOH are present in the reprocessed target solution and molten hydroxide salts can tolerate any moisture impurities in the dried NaOH, KOH, and K_2MoO_4 mixture.

2. EXPERIMENTAL

2.1 CHEMICALS AND METHODS

All chemicals were used as received from the manufacturer without additional purification. Tetrachloroethylene (TCE), 99% was obtained from Alfa Aesar. Tributyl phosphate (TBP), 97% was obtained from Sigma-Aldrich. Trace-metal grade hydrochloric acid (HCl) and trace-metal grade ammonium hydroxide (NH_4OH) were obtained from Fisher Scientific. MilliQ water (18 MΩ·cm) was used for the preparation of all solutions.

For electrochemical experiments, the molten salt was composed of a eutectic mixture of NaOH (Sigma-Aldrich, >98 % Anhydrous Redi-dry) and KOH (Beantown Chemical, > 99.95 %).

Two simulant solutions were prepared (Table 2), representing the maximum component concentrations expected in the two waste streams. These simulant solutions were used for all solvent extraction and electrochemical experiments.

Table 2. Simulant solutions A and B were prepared at two different chemical compositions. Metal constituents (Mo, Na, K) were verified by ICP-MS. Concentrations measured by ICP-MS are within ±10% of their reported values.

Chemical	Concentration (mol/L)	
	Simulant A	**Simulant B**
NaOH	1.92	2.34
Mo	0.190	0.0211
NaCl	6.14×10^{-2}	5.70×10^{-2}
KOH	5.72×10^{-1}	6.85×10^{-2}
KNO_3	1.30×10^{-2}	1.56×10^{-3}
NaClO	2.57×10^{-5}	3.08×10^{-6}

2.1.1 Solvent Extraction

The 30 vol% TBP in TCE solution was prepared in a graduated cylinder. Simulant solutions A and B were prepared in acid-washed, 1-L volumetric flasks. The general procedure used for solvent extraction experiments is shown below.

General Procedure

1. Feed solution (acidification):
    a. Acidify 20 mL of Simulant A solution using 20.92 mL concentrated HCl.

2. Extraction (5 M HCl):
    a. Aliquot 5 mL of 30% TBP/TCE to a glass test tube (Pyrex glass culture tubes w/ PTFE liners, 9826-16).
    b. Aliquot 5 mL of the feed solution to each vial.
    c. Mix vigorously for 3 minutes and allow to separate for 3–5 min.
    d. Separate entire phase by transfer pipet.
        i. Subsample 1 mL of one aqueous raffinate.

3. Scrub (4 M HCl):
    a. Aliquot 5 mL of scrub phase to each vial containing organic phase.
    b. Mix vigorously for 3 minutes and allow to separate for 3–5 minutes.
    c. Separate entire phase by transfer pipet.
        i. Subsample 1mL of one aqueous raffinate.

4. Strip (10% NH_4OH):
    a. Add strip solution to the vial.
    b. Separate by centrifugation for 3 minutes @ 24 *x* g.
    c. Subsample 1 mL of each aqueous (polystyrene tubes) and organic phase (glass vials).

For experiments with the Mo-99 radiotracer, the radiotracer was obtained from a commercial Mo-99/Tc-99m generator TechneLite (Lantheus Medical Imaging) milked with 1 M NH_4OH. Gamma counting of Mo-99 radiotracer samples was performed on an Ortec HPGe detector. Mo-99 was quantified using the 739 keV peak. Spectra were analyzed using GammaVision or PeakEasy (ver. 4.99) software.

Additional metal analysis (Na, K, Mo) was performed by ICP-MS using a NexION-2000-ICP-MS spectrometer (PerkinElmer). The instrument was calibrated with reference samples prepared by diluting National Institute of Standards and Technology-traceable standardsolutions procured from Agilent (Santa Clara, California, USA).

2.1.2 Electrochemistry

The experiments used 100–150 g of eutectic NaOH-KOH contained within an alumina crucible (AdValue Technology). To that mixture, 2–3 g of the dried waste solution was added. The crucible was sealed within a custom-built electrochemical reaction vessel, placed under vacuum, and heated to the test temperature of 185 ± 5 °C to dry the mixture and remove any dissolved moisture. The reaction vessel was backfilled with ultra-high purity argon and placed under a dynamic flow of 100 mL min^{-1} argon.

The electrochemical measurements were performed using a 304 stainless-steel plate working electrode, a graphite rod counter electrode, and either a tungsten or Mo wire reference electrode. Electrochemical measurements were performed using a Gamry 5000E. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) were performed using a Hitachi S-3400N with a Bruker EDS detector.

3. RESULTS

3.1 SOLVENT EXTRACTION

The existing scheme using a 10-stage flowsheet for Mo recovery was used as the template for waste stream processing. The first step in this process was the adjustment of the aqueous stream to 5 M HCl. During this point in the processing of the source solutions, the solubility limit of KCl was reached and a significant portion of the K^+ was removed by filtration of the KCl precipitate. However, during the acidification of the waste stream simulant solutions, no KCl precipitate formed because of the lower Mo and K^+ concentrations, and no filtration was needed. The resulting NaCl concentration (~1 M) from the acidification of NaOH was well within its solubility limit and did not precipitate [2].

3.1.1 Effect of NaOCl in Dilute and Concentrated Streams

The potential effects of NaOCl concentrations on the performance of the MOEX process to recover Mo was examined during acidification, extraction, scrub, and strip. The acidified waste streams with and without NaOCl were observed for signs of chemical reactions, such as the one producing chlorine gas:

$$NaClO + 2HCl \longrightarrow NaCl + Cl_2\,(g) + H_2O$$

Table 3 shows the volumetric constituents of each sample tested alongside the percentage of Mo recovered in the final strip (product) solution.

Table 3. Results from the acidification of waste streams to 5M HCl, extraction into 30%-TBP/TCE, and stripping with 22% NH_4OH. Conditions tested included the addition of fresh bleach, the addition of no bleach, and waste stream dilution.

	Volume (mL)					Mo-99 Recovered	
	Waste stream	NaOCl	Water	HCl	Mo-99 spike in water	(µCi)	(%)
Simulant A (no NaOCl)	5.00	0	0	5.23	0.050	46.8	98%
Simulant B (no NaOCl)	5.00	0	0	5.19	0.050	48.6	101%
Simulant A (w/ NaOCl)	5.00	0.0130	0	5.23	0.050	49.0	102%
Simulant B (w/ NaOCl)	5.00	0.0015	0	5.19	0.050	46.6	97%
Simulant A (no NaOCl, dilute)	3.00	0	2.00	5.23	0.050	45.6	95%
Simulant B (no NaOCl, dilute)	3.00	0	2.00	5.19	0.050	46.5	97%
Control	0	0	5.00	5.23	0.050	47.7	99%
Mo-99 spike only	-	-	-	-	0.050	48.0	-

In summary, Mo-99 recovery rates across various simulants and conditions hovered around 100%, with the presence of NaOCl and dilution causing no significant deviations. Both simulant solutions, irrespective of NaOCl presence, exhibited consistent behavior during acidification. The addition of NaOCl had a negligible effect on Mo recovery. Given the very small concentrations of NaOCl in the waste streams, no noticeable reactions, such as bubble formation signaling the release of Cl_2 gas from OCl^- reactions, were observed during acidification. While there's a potential for minor Cl_2 formation during acidification, the use of concentrated HCl in these steps meant that Cl_2 off-gassing was expected. Thus, any additional precautions due to OCl^- presence should be minimal.

3.1.2 Decontamination from Na and K

Early batch extractions showed nearly quantitative Mo recovery from all tested streams when using 20–22% NH_4OH as the strip phase. However, the precipitation of solids was observed during the strip step. Mo recoveries were unaffected by solid formation, so the solids were not Mo-containing salts. But solids interfere with large-scale contactor processing, therefore solid formation must be avoided. Preliminary testing found that solids formed when using ≥15% NH_4OH and no solids formed at ≤10% NH_4OH. This precipitation, discussed in more depth in Section 4.1.3, is likely due to the formation of NH_4Cl resulting from the neutralization reaction of HCl and NH_4OH. The experiments in this section used 10% NH_4OH as the strip condition to avoid precipitation.

Results for metal concentrations (Na, K, Mo) and percent recoveries/removals during each stage of the recycle process are given in Tables 4 and 5. In both simulant solutions, over 99% Mo was extracted (<1% in raffinate). Scrubbing with 4 M HCl led to 1.5% Mo loss for Simulant A and 0.7% Mo loss for Simulant B, leaving ~98–99% Mo in the organic phase after the scrub for both streams.

Table 4. Elemental profiles of Mo, Na, and K in <u>Simulant A</u> during acidification, extraction (1×), scrub (1×), and stripping (1×). Concentrations measured by ICP-MS are within ±10% of their reported values.

	Waste stream	**Feed (acidified waste stream)**		**Extraction Raffinate**		**Scrub Raffinate**		**Strip**	
	µg/L (ppb)	µg/L (ppb)	%	µg/L (ppb)	%	µg/L (ppb)	%	µg/L (ppb)	DF
Mo	1.82×10^{7}	9.18×10^{6}	100	5.34×10^{4}	0.6	1.42×10^{5}	1.5	7.84×10^{6}	
Na	4.45×10^{7}	2.26×10^{7}	100	2.27×10^{7}	100	2.67×10^{5}	1.2	8.47×10^{3}	4.4×10^{-4}
K	3.07×10^{7}	1.59×10^{7}	100	1.60×10^{7}	101	1.84×10^{5}	1.2	8.59×10^{3}	6.3×10^{-4}

DF = decontamination factor

Table 5. Elemental profiles of Mo, Na, and K in <u>Simulant B</u> during acidification, extraction (1×), scrub (1×), and stripping (1×). Concentrations measured by ICP-MS are within ±10% of their reported values.

	Waste stream	**Feed (acidified waste stream)**		**Extraction Raffinate**		**Scrub Raffinate**		**Strip**	
	µg/L (ppb)	µg/L (ppb)	%	µg/L (ppb)	%	µg/L (ppb)	%	µg/L (ppb)	DF
Mo	2.02×10^{6}	1.08×10^{6}	100	2.80×10^{3}	0.3	7.42×10^{3}	0.7	9.16×10^{5}	
Na	5.14×10^{7}	2.76×10^{7}	100	2.58×10^{7}	93	1.04×10^{6}	3.8	2.90×10^{4}	1.2×10^{-3}
K	3.70×10^{6}	2.08×10^{6}	100	2.04×10^{6}	98	7.28×10^{4}	3.5	2.50×10^{3}	1.4×10^{-3}

DF = decontamination factor

It was discovered that only 85% Mo was recovered from each stream during the strip stage because of incomplete phase disengagement. The lower strip concentration (10% NH_4OH) was chosen to avoid salt formation during stripping. It was later verified that longer centrifugation times were needed for complete phase separation at lower NH_4OH concentrations and that this was a probable cause for incomplete stripping. Stripping was improved to 99+% Mo recovery for all remaining experiments by improving phase disengagement.

Overall decontamination factors for Na and K were excellent for a flowsheet with a single stage of extraction, scrub, and strip. Mo recovery can be improved by optimizing the strip efficiency for a 10% NH_4OH strip, which is demonstrated in the following section.

3.1.3 Effects of Strip Conditions on Mo Recovery and Phase Behavior

Previous experiments showed that solid formation occurred during stripping when concentrated NH_4OH was used. When lower NH_4OH concentrations are used, the salt solubility increases and solid formation does not occur, but the dependence of Mo strip efficiency versus NH_4OH concentration is not known. Coextraction of acid in the organic phase can lead to the co-stripping of acid and partial neutralization of the strip phase. Additionally, conversion of Mo from $MoO_2^{2+} \rightarrow MoO_4^{2-}$ liberates four acidic protons, also reducing the strip pH. Strip efficiency can be expected to decrease at some pH. Mo strip efficiency was tested against strip conditions ranging from 8–22% NH_4OH. Phase behavior was also examined to determine the impact of strip conditions on solid formation.

Results are shown in Table 6. All organic phases were cloudy after initial phase disengagement. Cloudiness in the organic phase was resolved by sample centrifugation for 3 min @ 24 × g. The strip efficiency in prior experiments was 85% Mo for both Simulants A and B (using 10% NH_4OH) when a shorter pulse centrifugation was used. Longer centrifugation improved strip efficiency to 98–101% Mo over the entire range of NH_4OH tested (8–22%).

After centrifugation, all organic phases were clear, except in the 22% (concentrated) NH_4OH strip condition, where solids were present at the interface before and after centrifugation. Gamma counting of the organic phase resulted in no detectable Mo-99 activity with a detection limit equal to <0.05% cumulative Mo losses among all samples, implying quantitative Mo strip from the organic phase.

Table 6. Mo extraction results after contact with varying strip phases from 8–22% NH4OH. The organic phase was extraction Mo (from 4 M HCl) in 30% TBP/TCE.

Sample	Mo-99 (µCi)	Mo-99 (%)	Notes (Stripping behavior)
Acidified Feed	2.76	-	-
8% NH_4OH strip	2.77	100%	Excellent separation with centrifugation
11% NH_4OH strip	2.79	101%	Excellent separation with centrifugation
14% NH_4OH strip	2.77	100%	Excellent separation with centrifugation
17% NH_4OH strip	2.70	98%	Excellent separation with centrifugation
22% NH_4OH strip	2.71	98%	Solids on interface after centrifugation
All combined org phases	<0.0014	<0.05%	-

Varying the strip conditions did not impact Mo recovery despite the partial neutralization of the NH_4OH strip by any coextracted acid or by conversion of MoO_2^{2+} (molybdenyl) to MoO_4^{2-} (molybdate). The salt precipitate that forms during the strip was avoided by reducing the strip conditions to 8–17% NH_4OH without affecting Mo recoveries. The arbitrary concentration of 10% NH_4OH can be safely selected as the strip condition, providing adequate OH- to keep pH high while also keeping NH_4Cl in solution.

Figure 1 shows a photo of the solids that formed at the interface during stripping with 22% NH_4OH. The precipitation of solids indicates that aqueous molar concentrations of salts are too high. This can be altered by increasing the water content in the strip (i.e., reducing NH_4OH concentration) to avoid precipitation. Solid formation did not affect Mo recoveries, but will affect larger scale batch or continuous Mo recovery processing.

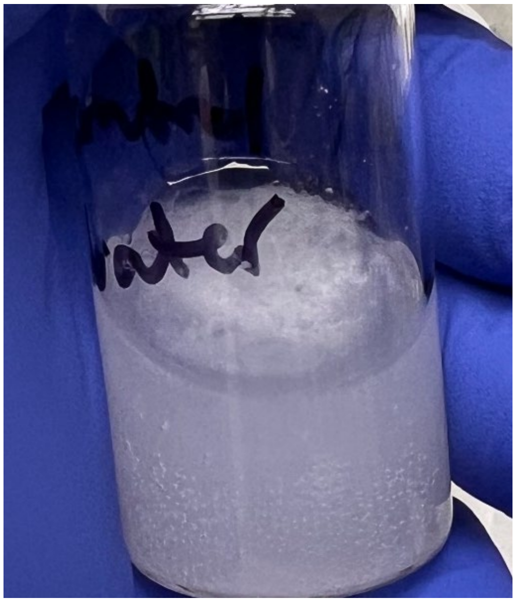


Figure 1 – A picture of salt (possibly NaCl/NH_4Cl) precipitating in the organic phase and interface during stripping with concentrated NH_4OH. The aqueous phase was removed and is not shown.

3.1.4 Modified Processing Scheme

Based on the laboratory-scale experimental results for the solvent extraction of LSA Mo-99/Tc-99m waste streams, a few slight modifications to the original MOEX flowsheet were identified, allowing for the > 99% recovery of Mo. Figure 2 shows an abbreviated diagram of the original MOEX scheme and the proposed modified scheme showing a lower NH_4OH concentration in the strip regime.

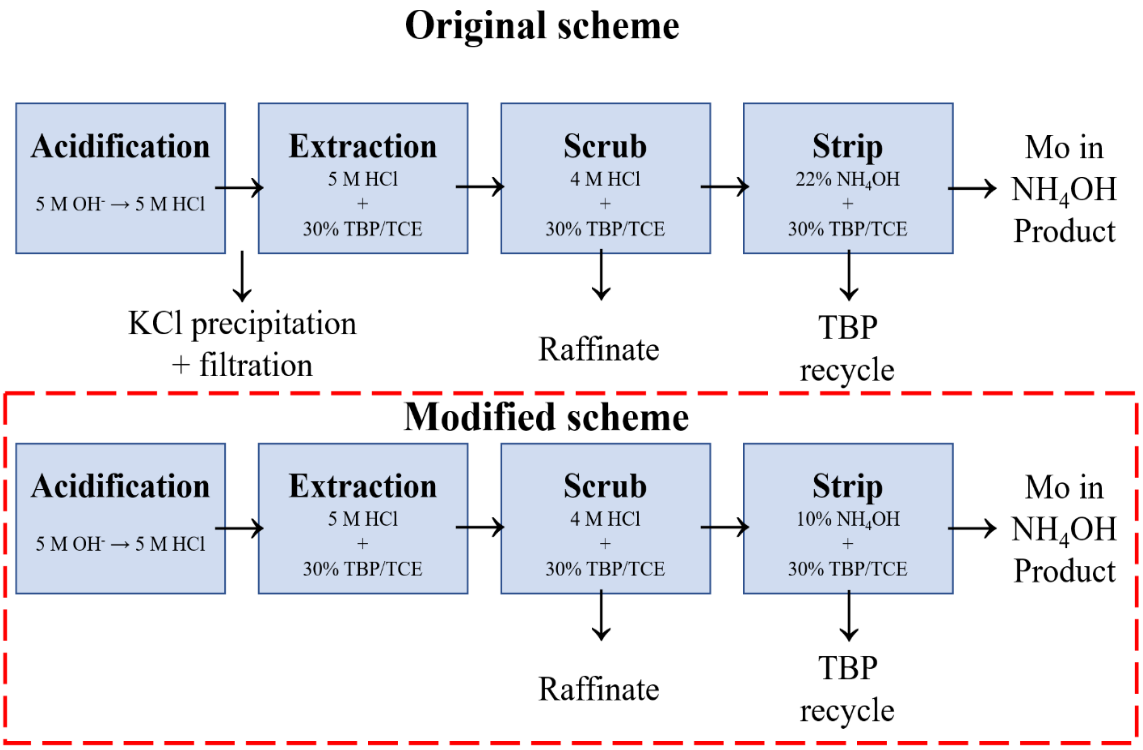


Figure 2 – Top - the original MOEX scheme (adapted **from reference 2). Bottom - the modified scheme for recycling of Mo from waste streams.**

The chemistry behind the extraction and stripping of Mo in the original MOEX stream is robust for a large range of metal impurities in the feed matrix. The two process changes needed to recycle Mo from waste solutions account for the solubility differences of chloride salts that form during the feed preparation and stripping phases, which only affected solution characteristics and did not impact Mo recoveries.

3.2 ELECTROCHEMISTRY

Molten NaOH-KOH was chosen as the electrochemical medium for its previously mentioned solubility of oxides and its compatibility with the waste streams. An industrial electrochemical recovery process would involve batch processing modules consisting of commercial-grade materials that could be employed at scale depending on the throughput needs and footprint of an industrial facility. Towards that end, electrochemical testing employed a single reactor vessel utilizing commercial steels and graphite immersed in a batch of salt loaded with 2–3 wt % of waste solution to assess the feasibility of recovering Mo from the waste solution.

3.2.1 Electrochemical Characterization

Electrochemical characterization of the Mo species dissolved in the molten salt was done using cyclic voltammetry on a 304 stainless-steel plate working electrode. A cyclic voltammogram of the steel plate in the NaOH-KOH-Mo salt is shown in Figure 3. In this test, the potential was swept at 50 mV s^{-1} from 0 V vs. Mo, which is equivalent to the equilibrium conditions of pure Mo metal, to -0.6 V vs. Mo before sweeping back to 0.45 V vs. Mo. Three features are visible in the scan: 1) a shoulder at approximately -0.45 V vs. Mo, labeled R1; 2) an oxidation peak at -0.046 V vs. Mo, labeled O1; and 3) the production of sodium metal at potentials more negative of -0.5 V vs. Mo. These electrochemical features suggest that R1 may be the reduction of dissolved K_2MoO_4 and that the production of sodium metal would likely occur as a coreduction product because of the overlap in potentials between R1 and sodium reduction.

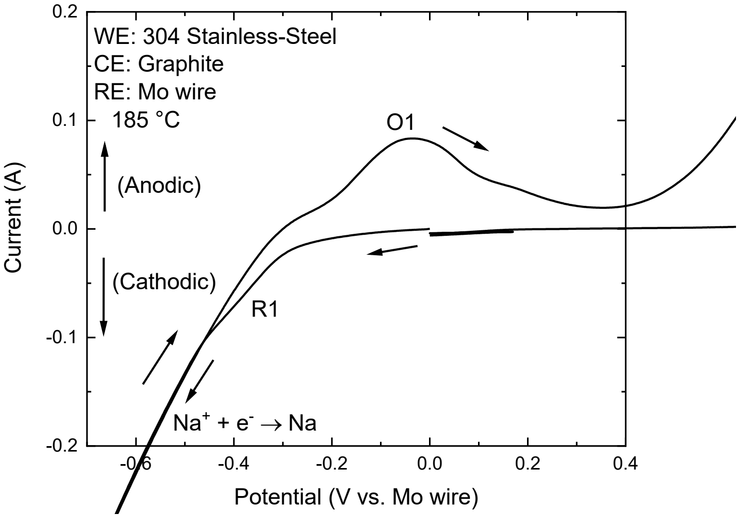


Figure 3 – Cyclic voltammogram of a stainless-steel plate in the NaOH-KOH-Mo salt swept at 50 mV s^{-1}.

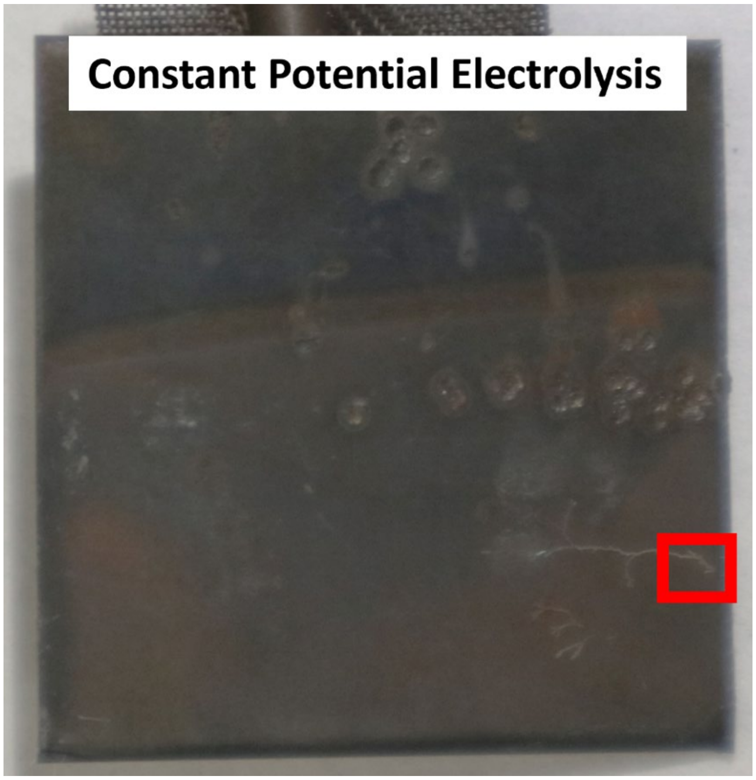
3.2.2 Electrolysis Tests and Characterization

Two reduction tests were performed in the NaOH-KOH-Mo mixture to assess the feasibility of electrochemically extracting Mo metal from the melt. First, a constant potential of -0.45 V vs. Mo was applied to a steel plate working electrode for 2 h. This potential was chosen because it is more reducing than the R1 feature from Figure 3 to verify if R1 is associated with Mo deposition. Second, a constant current of -25 mA was applied across the cell for 6 h. The low current was chosen to evaluate if the R1 feature was associated with potentially kinetically slow Mo deposition.

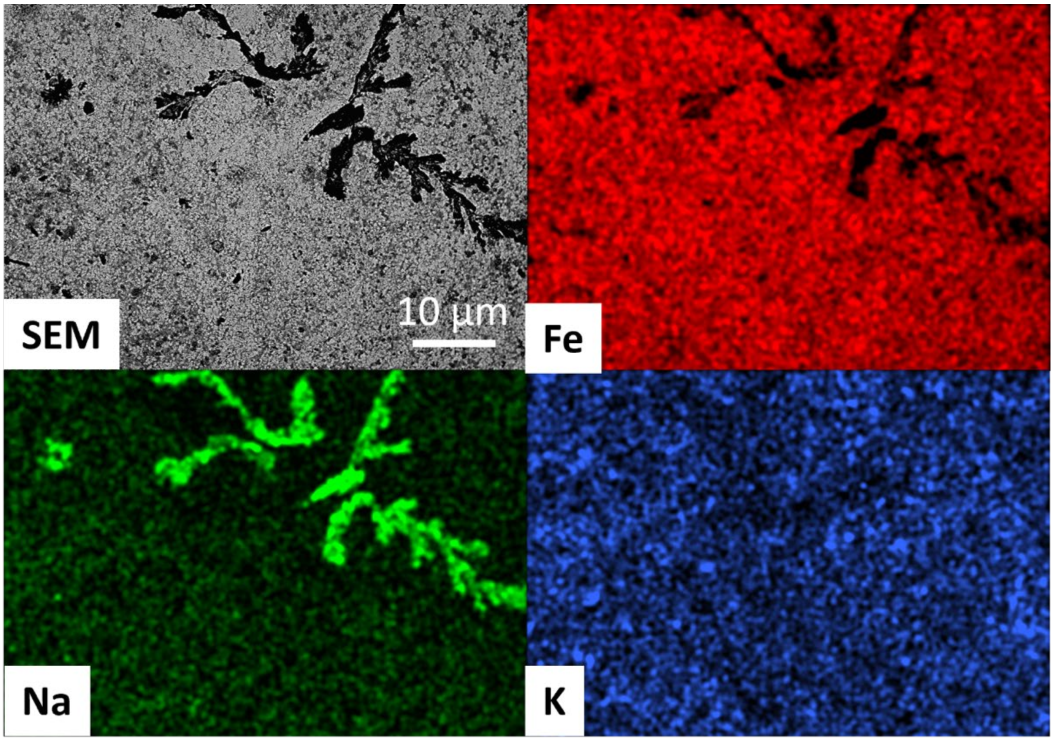
After the tests were complete, the steel plates were removed from the salt, the reaction vessel was cooled down, and the electrodes were isolated and washed. The NaOH-KOH-Mo salt had a pale-yellow color, indicating that the waste solution dissolved in the melt. Pure NaOH-KOH eutectic is white. The rinsed electrode from the constant potential electrolysis test is shown in Figure 4a and the rinsed electrode from constant current electrolysis test is shown in Figure 5a. Both of the electrodes pictured in Figures 4a and Figure 5a had strongly adhered yellow salt that was not easily removed by rinsing. A small area of metal deposition was observed on both electrodes.

A dendritic deposit was observed in Figure 4a near the marked red area and a nodule was observed in Figure 5a near the marked red area. Samples were taken from the stainless-steel plate electrodes for characterization by SEM-EDS. The portion of the electrodes that were imaged are outlined in red in Figures 4a and 5a. The EDS mappings for both samples are given in Figures 4b and 5b. The bright green mapping for sodium in both maps shows sodium metal was deposited on the surface of the steel electrode. No bright spots are present in Figure 4b for potassium, indicating it did not deposit under constant potential conditions. Figure 5b shows some bright spots in the blue mapping associated with potassium deposition from constant current deposition. Area scans of the samples measured approximately 0.1 atom% Mo content, indicating that significant Mo deposition did not occur.

As discussed earlier, the potentials associated with the reduction of Mo and Na are quite similar and coreduction was likely to occur. Sodium is a primary constituent of salt and the waste product, it is a single electron reduction, and its reduction is thermodynamically similar to Mo. The combination of these factors leads to significant Na deposition and minimal Mo deposition.

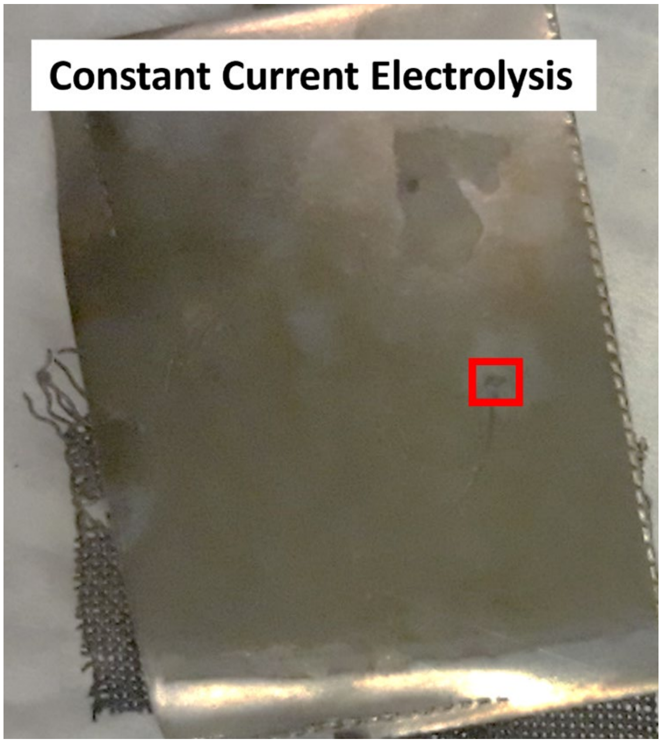


(a)

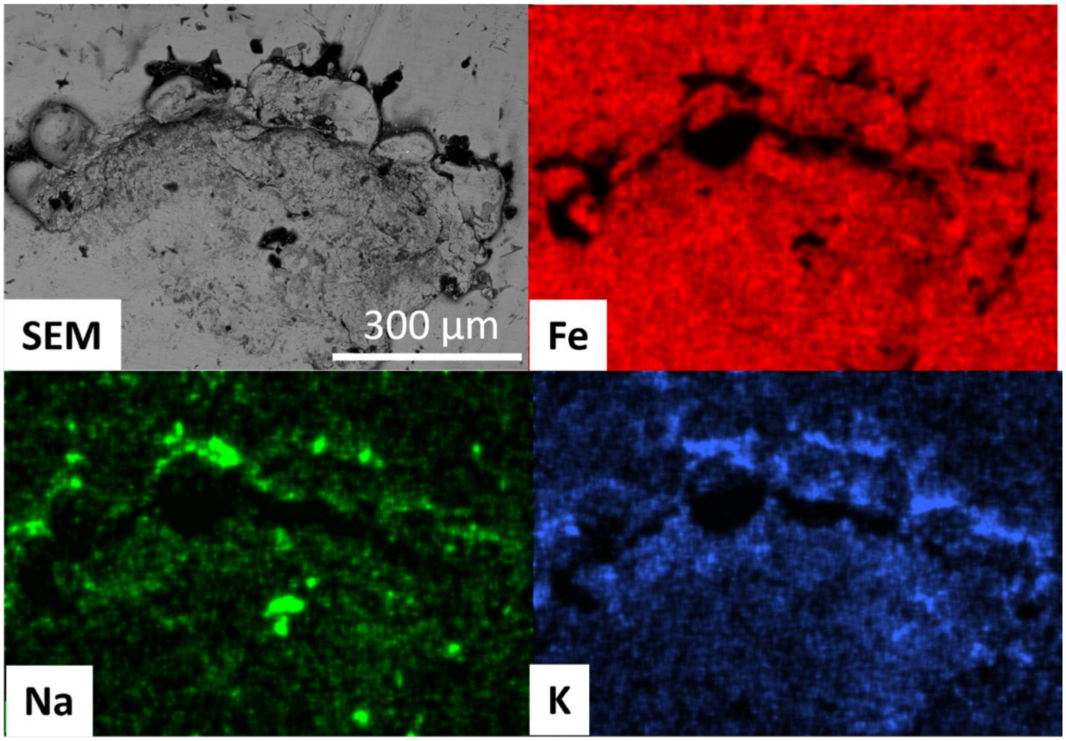


(b)

Figure 4 – A photograph (a) and a photomicrograph (b) with EDS mapping for the recovered cathode from constant potential electrolysis.



(a)



(b)

Figure 5 – A photograph (a) and a photomicrograph (b) with EDS mapping for the recovered cathode from constant current electrolysis.

4. CONCLUSIONS

Two simulant solutions, representing the extremes of Mo/impurities in LSA Mo-99/Tc-99m waste streams, were employed to assess the viability of both solvent extraction and electrochemical techniques for the pure Mo recovery intended for recycling.

In the solvent extraction approach, simulant waste streams underwent acidification using HCl to produce the feed solution. The extraction and recovery of Mo was nearly quantitative, with high decontamination factors for both Na and K (10^3–10^4) after a single extraction, scrub, and strip stage. Adopting a 10-stage flowsheet (3× extraction, 4× scrub, 3× strip) is projected to yield high-purty Mo. To prevent chloride salt precipitation during the strip phase, the strip condition was adjusted from 22% to 10% NH_4OH. This modification had no discernible impact on Mo recovery.

Regarding the electrochemical technique, a segment of waste Simulant A was evaporated, with the residual matter assessed in a NaOH-KOH melt. This melt contained 2–3-g of the Simulant A product and was maintained at 185°C. The 304 stainless-steel plate was tested as the recovery electrode. During electrochemical characterization, a redox couple was detected at potentials slightly more positive than sodium deposition. This indicates the dissolution of redox-active species in the salt. Both constant potential and constant current electrolysis conditions were explored for Mo metal recovery. However, neither exhibited significant Mo metal deposition. While there's indicative evidence of K_2MoO_4 dissolution into the melt, alternative molten salts or electrode materials might be necessary for the electrolytic recovery of Mo.

5. ACKNOWLEDGEMENTS

The work described in this report was supported by the U.S. Department of Energy, National Nuclear Security Administration's Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.

6. REFERENCES

1. Bettinardi, David J.; Servis, Anna G.; Tkac, Peter. "Removal of Tc-99, Zr-95, and Nb-95, From Solutions Obtained After Dissolution of Irradiated Mo Targets." Argonne National Laboratory (ANL), Lemont, IL (United States), September 2022. Report Number: ANL-22/63. Available: https://www.osti.gov/biblio/1892075.

2. P. Tkac, M. A. Brown, A. Momen, K. E. Wardle, J. M. Copple, and G. F. Vandegrift, "MOEX: Solvent extraction approach for recycling enriched 98Mo/100Mo material," Separation Science and Technology, vol. 53, no. 12, pp. 1856–1863, 2018.

3. D. Bettinardi and P. Tkac, “Recycling Isotopically Enriched Mo from the RadioGenix Waste Stream,” Argonne National Lab. (ANL), Lemont, IL, Technical Report ANL-20/20, Mar. 01, 2020. [Online]. Available: https://www.osti.gov/biblio/1604883

4. P. Kozak, B. Saboriendo, and P. Tkac, “Additive Manufacturing Fabrication of PEEK Counter-Current Centrifugal Contactor Components,” Argonne National Lab. (ANL), Lemont, IL, Technical Report ANL/CFCT-19/22, Oct. 23, 2019. [Online]. Available: https://www.osti.gov/biblio/1596336

5. D. Inman and S. H. White, “The production of refractory metals by the electrolysis of molten salts; design factors and limitations,” J. Appl. Electrochem., vol. 8, pp. 375–390, 1978.

6. A. Patra et al., “Electrodeposition of atmosphere-sensitive ternary sodium transition metal oxide films for sodium-based electrochemical energy storage,” PNAS, vol. 21, no. 22, e202504418, 2021.

7. A. Cox and D. J. Fray, “Electrolytic formation of iron from haematite in molten sodium hydroxide,” Ironmaking and Steelmaking, vol. 35, no. 8, pp. 561–566, 2008.

Chemical and Fuel Cycle Technologies Division
Argonne National Laboratory
9700 South Cass Avenue
Lemont, IL 60439-4832

www.anl.gov