

Influence of Temperature on Precipitates and Mo Uptake in Alkaline Fission ⁹⁹Mo Dissolution

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1. Introduction

Molybdenum-99 (⁹⁹Mo) is the parent radionuclide of technetium-99m (^{99m}Tc), which is widely used in nuclear medicine [1]. KAERI is developing a fission ⁹⁹Mo production process using a low-enriched uranium target. The process includes a target dissolution step using a concentrated alkaline solution, followed by separation and purification steps [1,2]. Under concentrated alkaline conditions, Mo is mainly present as anionic molybdate and can be retained by strong basic anion-exchange resins [3,4].

In this study, the effect of temperature on Mo uptake by a strong basic anion exchange (SBA) resin was evaluated. The characteristics of precipitates observed during cooling of the target dissolution liquor were also investigated. The aim was to identify a suitable cooling condition for the separation step.

2. Experimental

2.1. Batch Mo uptake test

SBA resin in the chloride form was conditioned with 1 M NaOH for 5 min and washed three times with deionized water. Approximately 50 mg of vacuum-filtered wet resin (49.5–50.8 mg; target tolerance ±5%) was transferred to each of two replicate vials. Each vial received 10 mL of a nominal 40 ppm Mo solution prepared in a concentrated alkaline solution. Samples were mixed at 180 rpm for 1 h at incubator set temperatures of 30, 40, 50, and 60 °C. After 1 h, the resin was removed by syringe filtration, and the residual Mo concentration was measured by ICP-MS. The apparent Mo uptake was calculated for each replicate using the following equation:

$$q_e = \frac{(C_i - C_e)DV}{1000m}$$

where q_e is the apparent Mo uptake after 1 h (mg Mo g⁻¹ wet resin); C_i and C_e are the initial and residual ICP-MS concentrations measured after analytical dilution, respectively (μg L⁻¹); D is the analytical dilution factor ($D = 600$); V is the solution volume (0.010 L); and m is the actual wet-resin mass (g). The factor of 1000 converts μg g⁻¹ to mg g⁻¹. Results are reported as the mean and sample standard deviation of duplicate measurements.

2.2. Cooling and precipitate characterization

An alkaline target dissolution liquor was cooled from 90 °C. At 65, 55, 45, 35, and 25 °C, 100 mL aliquots were collected and vacuum-filtered through 10 μm filter paper.

The recovered solids were washed and dried before SEM-EDS analysis.

3. Results and Discussion

3.1. Effect of temperature on Mo uptake

The apparent Mo uptake values (q_e) at 30, 40, 50, and 60 °C were 0.54 ± 0.11 , 0.92 ± 0.22 , 1.73 ± 0.11 , and 1.18 ± 0.50 mg g⁻¹ wet resin, respectively. Among the tested temperatures, 50 °C gave the highest q_e and the smallest relative variation between duplicate measurements. At 60 °C, q_e decreased and the duplicate variation increased. The decrease at 60 °C may be related to thermal instability of the resin under the concentrated alkaline condition. The 50 °C condition was selected for further process evaluation.

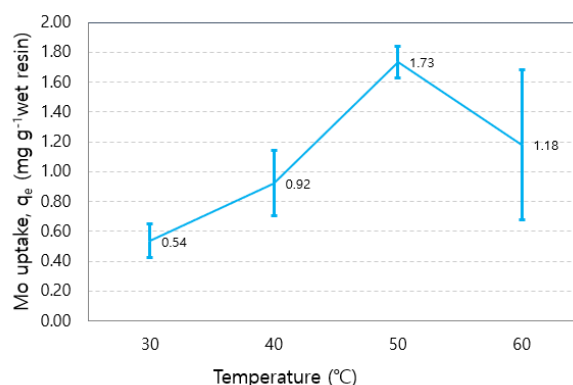


Fig. 1. Effect of temperature on Mo uptake by the SBA resin. Error bars represent the standard deviation of duplicate measurements ($n = 2$).

3.2. Precipitate evolution during cooling

At 65 and 55 °C, black, brown, and gray regions were clearly visible on the filter papers (Fig. 2). For each color, the most visually distinct area was cut from the filter paper and analyzed by SEM-EDS. The precipitates collected at 45, 35, and 25 °C showed no clear color distinction, so representative areas were analyzed without color classification. EDS values are reported as local weight percentages for the analyzed areas.

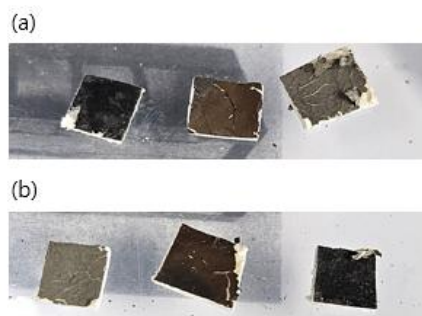


Fig. 2. Representative black, brown, and gray precipitate regions collected at (a) 65 °C and (b) 55 °C during cooling of the target dissolution liquor.

From the black to brown and gray regions, the Na content decreased, whereas Mg, Al, Fe, Cr, Mn, and Cu generally increased. The black regions were Na-rich (approximately 33–35 wt%), whereas Mg, Al, and Fe, which are major impurity-related components, were more prominent in the brown and gray regions. At 45, 35, and 25 °C, the representative areas showed low Na contents and similar Mg-Al-Fe compositions (Table I).

Table I. Selected elemental EDS spot compositions of black, brown, and gray precipitate regions at 65 and 55 °C and representative precipitate areas at 45, 35, and 25 °C (wt%)

Temperature / region	Na	Mg	Al	Fe
65 °C / black	34.55	0.00	1.77	0.25
55 °C / black	33.00	0.04	0.92	0.24
65 °C / brown	20.39	4.83	4.62	1.99
55 °C / brown	25.38	2.17	5.61	1.53
65 °C / gray	7.63	12.33	7.60	4.77
55 °C / gray	2.88	12.89	7.54	7.84
45 °C / gray	0.34	15.46	8.29	6.99
35 °C / gray	2.70	13.07	8.05	5.02
25 °C / gray	0.08	14.46	7.53	6.55

Table II summarizes the expected major species of the selected elements relevant to precipitate interpretation at pH 14, together with their qualitative precipitation tendencies during cooling.

Table II. Expected major species of selected elements at pH 14 and their qualitative precipitation tendencies during cooling.

Element	Major species (pH 14)	Cooling-related precipitation tendency
B	B(OH)_4^-	Low
Si	H_2SiO_4^- , SiO_3^{2-}	Conditional
Al	Al(OH)_4^-	Low
Mg	$\text{Mg(OH)}_2(\text{s})$	High-temperature precipitation
Fe	Fe(OH)_3 / FeOOH / Fe oxide	High-temperature precipitation
Cu	Cu(OH)_2 / CuO	Precipitate / oxide
Cr	Cr(OH)_4^- , CrO_4^{2-}	Conditional
Zn	$[\text{Zn(OH)}_4]^{2-}$	Low

The listed species were considered for interpretation of the EDS results and were not directly measured in the solution.

Mg, Al, and Fe were already present in the gray precipitate regions at 65 and 55 °C, and similar compositions were maintained in the representative areas at 45, 35, and 25 °C. The main Mg-Al-Fe-rich precipitates were therefore considered to have formed in the higher-temperature region. Little additional formation of a major precipitate phase was expected during further cooling below 45 °C. This interpretation is based on local EDS composition and does not quantify the total precipitate mass.

4. Conclusion

Among the temperatures tested, 50 °C gave the highest Mo uptake and the smallest relative variation between duplicate measurements. At 60 °C, Mo uptake decreased and duplicate variation increased. The decrease at 60 °C may be related to thermal instability of the resin under the concentrated alkaline condition. SEM-EDS showed similar Mg-Al-Fe compositions in representative precipitate areas at 45, 35, and 25 °C, and these elements were also observed in gray precipitate regions at 65 and 55 °C.

Cooling a large feed volume increases the processing time and may reduce the recoverable ^{99}Mo activity through radioactive decay. Precipitates in the feed may contribute to fouling, while elevated temperature may reduce resin stability. The feed temperature for further process evaluation was therefore set at 50 °C.

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