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Nuclear Engineering Division

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Argonne is assisting SHINE Medical Technologies (SHINE) in their efforts to develop an accelerator-driven process that utilizes a uranyl-sulfate solution for the production of fission Mo 99. In an effort to design a Mo-recovery system for the SHINE project using low-enriched uranium (LEU), we conducted batch, breakthrough, and pulse tests to determine the Mo isotherm, mass-transfer zone (MTZ), and system parameters for a 130 g-U/L uranyl sulfate solution at pH 1 and 80°C, as described previously.[1,2] The VERSE program was utilized to calculate the MTZ under various loading times and velocities. The results were then used to design Mo separation and recovery columns employing a pure titania sorbent (110-µm particles, S110, and 60 Å pore size). The plant-scale column designs assume Mo will be separated from 271 L of a 141 g-U/L uranyl sulfate solution, pH 1, containing 0.0023 mM Mo. The VERSE-designed recovery systems have been tested and verified in laboratory-scale experiments, and this approach was found to be very successful.

For the full-scale Mo recovery column, a 14 × 10 cm column utilizing S110 sorbent is proposed. Table 1 shows Mo recovery calculated for different column dimensions. The pressure drop, ΔP, for this design was calculated by the Ergun equation to be 0.14 atm. For recovery of Mo, the target irradiated uranyl sulfate solution is passed at a flow rate of 2258 mL/min for 120 min. The loading step is followed by a wash with 10 bed volumes (BVs) of 0.1 M H_2SO_4 to remove the remaining unadsorbed uranium and fission products from the column. The acid wash is followed by washing with 10 BVs of water before stripping the Mo with base solution. The Mo is removed from the titania sorbent by replacement of Mo with hydroxyl ions. Since the first step in the stripping process is a reaction of OH^- with protonated titania sites, the column is pretreated with 3 BVs of 1 M NaOH to facilitate the stripping process by adjusting the pH of the column. This step allows utilization of an overall smaller volume of solution in the stripping process. Subsequently, the Mo product is removed with 16 BVs of 0.1 M NaOH at 5 cm/min and 80°C to obtain 24.63 L of a 0.0253 mM Mo solution. The 0.1 M NaOH solution was chosen for the stripping step because it is compatible with the subsequent product concentration steps.

TABLE 1 SHINE column designs for recovery of Mo from 271 L of a 141 g-U/L uranyl sulfate solution containing 0.0023 mM Mo (pH 1)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)
10	28.75	16.76	18	1414	1838	0.50
12	19.97	12.56	14	1583	2058	0.27
14	14.67	9.20	10	1539	2001	0.14
15	12.78	8.41	9	1590	2068	0.11
20	7.19	5.44	6	1885	2450	0.04

For the 5 L mini-SHINE experiment conducted at the Argonne linear accelerator (LINAC), a 2-cm internal diameter × 10-cm length column design was used (Table 2). The 140 g-U/L uranyl sulfate solution at pH 1 containing 0.0023 mM Mo was loaded at 42 mL/min for 120 min at 80°C. For stripping of Mo, the sorbent was pretreated with 3 BVs of 1 M NaOH, followed by 27 BVs of 0.1 M NaOH, resulting in 940 mL of Mo product. The product was stripped at 5 cm/min and 80°C. In this mini-SHINE experiment, all 30 BVs of stripping solution were collected and processed to obtain a complete stripping profile for Mo under irradiation conditions.

TABLE 2 Mini-SHINE column designs for recovery of Mo from 5 L of a 140 g-U/L uranyl sulfate solution containing 0.0023 mM Mo (pH 1)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)
2	13.38	8.72	10	31	41	0.13

Further demonstration of Mo production at the Argonne LINAC will utilize 20 L of 140 g-U/L solution containing 0.0023 mM Mo. For this demonstration, the feed will be loaded at 168 mL/min for 120 min at 80°C on a 4 cm × 10 cm column with S110 sorbent (Table 3). The column will be pretreated with 3 BVs of 1 M NaOH, and the product will be subsequently collected by stripping with 16 BVs of 0.1 M NaOH.

TABLE 3 Mini-SHINE column design for recovery of Mo from 20 L of a 140 g-U/L uranyl sulfate solution containing 0.0023 mM Mo (pH 1)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)
4	13.38	8.72	10	126	163	0.13

To reduce the Mo product volume (25 L) from the recovery column for the subsequent LEU-modified Cintichem process, a Mo concentration process was developed. A concentration column using a titania sorbent (S40, 40 micron particles, and 60 Å pores) was designed, where a pH 2 loading solution was chosen as described previously.[3] Batch, breakthrough, and pulse tests were conducted to determine the Mo isotherm, MTZ, and system parameters at 80°C for a 0.1 M NaOH solution acidified with nitric acid to pH 2. The VERSE program was utilized to calculate the MTZ for loading Mo product solution containing 0.025 mM Mo, acidified to pH 2, for 60 min, at various velocities. The proposed full-scale Mo concentration column is 5 cm × 1 cm and loaded at 410 mL/min (Table 4). The pressure drop, ΔP, for this design was calculated by the Ergun equation to be 0.14 atm. The loading step is followed by a wash with 10 BVs of 0.01 M HNO_3 to remove the remaining unadsorbed impurities from the column. The acid wash is followed by washing with 10 BVs of water before stripping Mo with base solution. Subsequently, Mo is removed from the column with 16 BVs of 1 M NaOH at 5 cm/min and 70°C.

TABLE 4 SHINE concentration column designs for concentrating Mo from 24.63 L of product solution containing 0.025 mM Mo (pH 2)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)
4	32.67	0.95	1.5	19	24	0.34
5	20.91	0.63	1.0	20	25	0.14
6	14.52	0.44	1.0	28	36	0.10
8	8.17	0.27	0.5	25	32	0.03

For the 5 L mini-SHINE experiment conducted at the Argonne LINAC, a 1 cm × 1 cm column design was used (Table 5). The recovery-column product solution containing 0.012 mM Mo is acidified to pH 2 with 10 M HNO_3 and loaded at 16 mL/min for 60 min at 80°C. The Mo is stripped from the column with 30 BVs of 1 M NaOH at 70°C and 5 cm/min (4 mL/min). In the 5 L mini-SHINE experiment, 30 BVs (25 mL) of stripping solution is used to remove Mo from the column due to the large dead volume of the system (15 mL).

TABLE 5 Mini-SHINE concentration column design (5 L) for concentrating Mo from 0.94 L product solution containing 0.012 mM Mo (pH 2)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)
1	19.99	0.48	1.0	0.79	0.99	0.14

A concentration column was designed for the 20 L mini-SHINE demonstration at the Argonne LINAC. The Mo product from the recovery column is 2 L of 0.1 M NaOH solution containing 0.023 mM Mo. For this demonstration, the feed will be loaded at 34 mL/min for 60 min at 80°C on a 1.5 cm × 1 cm column with S40 sorbent (Table 6). The Mo is stripped from the column with 16 BVs of 1 M NaOH at 70°C and 5 cm/min (9 mL/min).

TABLE 6 Mini-SHINE concentration column design (20 L) for concentrating Mo from 2 L product solution containing 0.023 mM Mo (pH 2)

Column ID (cm)	Velocity (cm/min)	$MTZ_{0.1\%}$ (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	ΔP (atm)
1.5	18.96	0.56	1	1.77	2.23	0.13

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