Column Optimization Studies

Chemical Science and Engineering Division

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prepared for

U.S. Department of Energy, National Nuclear Security Administration,
Office of Defense Nuclear Nonproliferation

February 10, 2012

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COLUMN OPTIMIZATION STUDIES

1 INTRODUCTION

Argonne National Laboratory (Argonne) is assisting Babcock and Wilcox Technical Services Group (BWTSG) in their efforts to develop an aqueous homogenous reactor (AHR) for the production of molybdenum-99 (Mo-99). Several different titania-based sorbents and alumina have been investigated as potential candidates for the development of a separation and recovery column for Mo-99 from a uranyl nitrate solution. A pure titania sorbent with 80- μm particles and 60-Å pores (S80) was initially chosen for the plant-scale column. However, ZirChrom Separations, Inc., discontinued their Sachtopore (pure titania) sorbent with 80- μm particles and 60-Å pores. As a result, Argonne has tested several other Sachtopore sorbents with different particle and pore sizes in an effort to find a replacement for S80. Initial Versatile Reaction Separation (VERSE) column designs suggest that S40 is the best replacement for S80; however, experimental results show that a significant amount of Mo does not adsorb on the S40 sorbent. S110 performs much better than S40, and the S110 column designs are final designs for the plant-scale operation and the mini- Medical Isotope Production System (mini-MIPS).

2 BATCH STUDIES: EXPERIMENTAL

The uptake of Mo(VI) was determined by equilibrating 1 mL of a Mo-99 spiked aqueous solution with a known amount (10 ± 1 mg) of sorbent for 24 hours or 1–48 hours for kinetic tests at 60°C using a thermostated shaker bath. Aqueous solutions contained tracer Mo-99 and 1 ppm stable Mo added as $\text{Na}_2\text{MoO}_4 \cdot 2 \text{H}_2\text{O}$ in the presence of uranyl nitrate. After equilibration, the solution was withdrawn and filtered using a syringe fitted with a 0.22- μm pore size polyvinylidene fluoride (PVDF) membrane filter.

2.1 PREPARATION OF Mo-99 SPIKE SOLUTION

Mo-99 was obtained from a spent Tc-99m generator (provided by Hot Shots Nuclear Medicine), which we receive on a weekly basis. The initial activity of Mo-99 in a generator is typically between 1 and 10 Ci. However, we receive a Tc-99m generator when the activity remaining in the generator is insufficient for patient administration. Typically, a spent Tc-99m generator contains 0.1–0.3 Ci of Mo-99, which is more than enough for our tracer batch and column work.

Mo-99 was removed from the generator by placing a serum vial containing 1 M NH_4OH on the needle labeled “Saline Charge.” After that, an evacuated serum vial was placed on the needle labeled “Receiver.” When no more bubbles appeared in the Receiver vial, the Receiver bottle was removed from the generator. The Mo-99-spiked solution was prepared by bringing the solution to dryness on a hot plate, and re-dissolving it in 0.1-M HNO_3 .

2.2 COUNTING OF Mo-99

The amount of activity in the aqueous samples was determined using a germanium detector. Mo-99 was quantified by measurement of its 739 keV γ -ray. The activity of Mo-99 in each sample was corrected for decay. The extent of radionuclide uptake was expressed in terms of a distribution coefficient, K_d , shown in equation (1):

$$K_d = \left(\frac{A_o - A_s}{W} \right) \bigg/ \frac{A_s}{V} \quad (1)$$

Here, A_o and A_s represent the aqueous phase activity (μCi) before and after equilibration, respectively; W is the dry weight of the sorbent (g); and V is the volume of the aqueous phase (mL).

3 KINETICS

The uptake of Mo as a function of time was determined using a pure titania sorbent with different particle and pore sizes from solutions containing 90 g-U/L uranyl sulfate and 150 g-U/L uranyl nitrate. The pure titania sorbent with 110- μm particles and 60- $\text{\AA}$ pores (S110) performed the best. Mo uptake was fairly consistent using both 90 g-U/L uranyl sulfate and 150 g-U/L uranyl nitrate solutions after 1–40 hours of contact time using S110 sorbent. It appears that equilibrium has been reached after 40 hours using a 90 g-U/L uranyl sulfate solution; however, it may take 48 hours or more for equilibrium to be reached using a 150 g-U/L uranyl nitrate solution. S80(60) performed the next best; however, the uptake of Mo was much better from a solution containing 150 g-U/L uranyl nitrate compared to a solution containing 90 g-U/L uranyl sulfate. S40(60) performed similarly to S80(60) in the presence of 90 g-U/L uranyl sulfate. Sorbents with larger pore sizes behaved much worse. S80(300), S40(300), and S80 (500) adsorbed the least amount of Mo, and the kinetics were slower. These results suggest that using a titania sorbent with larger pore sizes will not be a good choice for the design of a Mo separation and recovery column. K_d values using titania sorbents with larger pore sizes are about 1000 times less after 20–48 hours of contact time. The effects of slower kinetics and decreased Mo adsorption are expected for solutions containing 150 g-U/L uranyl nitrate, as well. The results are shown in Figure 1.

FIGURE 1 Kinetic Data for the Uptake of Mo from Solutions Containing 90 g-U/L Uranyl Sulfate or 150 g-U/L Uranyl Nitrate Using Pure Titania Sorbent with Different Particle and Pore Sizes

4 COLUMN DESIGN

4.1 MINI-MIPS

Batch study data indicate that sachtopore sorbents with 40- and 110- μm particles and 60- $\text{\AA}$ pores are suitable for the design of a separation and recovery column for Mo-99 for mini-MIPS. As a result, batch study data were input into VERSE to generate column designs for S40 and S110. The mini-MIPS column design assumes a feed solution with a Mo concentration of 0.0045 mM in the presence of 0.0055-mM competing components. About 5 L of a 145 g-U/L uranyl nitrate solution (pH 1) will be loaded onto a column in 2 hours in the up-flow direction. Mo will be eluted in the down-flow direction using 1-M NH_4OH , and VERSE assumes 99% recovery. The pressure limit is set at 0.8 atmospheres. Table 1 shows the column designs for the mini-MIPS solution for S40, S80, and S110. Each column will have an internal diameter of 2.0 cm, but the minimum length that should be tested (as indicated by VERSE results) varies for each sorbent: S40—3.5 cm; S80—6.8 cm; and S110—9.8 cm. The loading velocities do not change and are set at 12.3 cm/min. Based on the results shown in Table 1, S40 appears to be the top candidate.

4.2 PLANT-SCALE OPERATION

Batch study data indicate that Sachtopore sorbents with 40- and 110- μm particles and 60- $\text{\AA}$ pores are suitable for the design of a separation and recovery column for Mo-99 for the plant-scale process. As a result, batch study data were input into VERSE to generate column designs for S40 and S110. The plant-scale column design assumes a feed solution with a Mo concentration of 0.0045 mM in the presence of 0.0055 mM competing components. Approximately 240 L of a 145 g-U/L uranyl nitrate solution (pH 1) will be loaded onto a column in 2 hours in the up-flow direction. Mo will be eluted in the down-flow direction using 1-M NH_4OH , and VERSE assumes 99% recovery. The pressure limit is set at 0.8 atm. Two different linear velocities (16.3 cm/min and 12.3 cm/min) and internal diameters (14.4 cm/min and 12.5 cm/min) were tested for each sorbent using VERSE. VERSE stripping results are shown in Figure 2. Table 2 shows the column designs for the plant-scale process for S40, S80, and S110. Again, results suggest that S40 would be the top candidate for the Mo-99 separation and recovery column because it would be the smallest column. The 14.4-cm ID $\times$ 3.5-cm L column design for S40 would be the smallest column, but the 12.5-cm ID $\times$ 4.6-cm L column design for S40 exceeds the pressure limit of 0.8 atm.

TABLE 1 Proposed Column Designs for MINI-MIPS 0.0045-mM Mo and 0.0055-mM Competing Ions in 145-g-U/L Uranyl Nitrate and 0.1-M Nitric Acid at 60°C (loading time = 2 hours, up-flow), 1-M NH₄OH Stripping for 99% Mo Recovery (down-flow)

Parameter	Mini-MIPS		
	S40	S80	S110
d_p (μm)	40	80	110
ID (cm)	2.0	2.0	2.0
$u_{s, loading}$ (cm/min)	12.3	12.3	12.3
L_{max} (cm) ^a	4.6	18.2	34.3
L_{min} (cm) ^a	1.7	3.4	4.9
Designs with min. L_{tested}			
Min. L_{tested} ^a (cm)	3.5	6.8	9.8
CV_{tested} (mL)	5	11	15
Flowrate (mL/min)	38.6	38.6	38.6
Feed Vol. (mL)	4636	4636	4636
ΔP (atm)	0.6	0.3	0.2
$W_{sorbent}$ (g)	7	14	20
Stripping ^b			
u_s (cm/min)	10.0	10.0	10.0
Vol. (mL)	41	103	164
Vol. (CV)	3.8	4.8	5.3
Time (min)	1.7	4.2	6.6

^a At a given velocity, L_{max} is the column length when pressure drop during loading is 0.8 atm; L_{min} is column length from column inlet to the leading edge of 0.1% $C_{f,Mo}$. The minimum L_{tested} has a safety factor of 2: a capture column with $L_{0.1\%C_{f,Mo}}$ and a guard column with $L_{0.1\%C_{f,Mo}}$.

^b The stripping step starts at the pH step change and lasts until 99% Mo is recovered.

FIGURE 2 Dimensionless Stripping Results of Sachtopore Sorbents with $d_p = 40$ (S40), 80 (S80), and 110 μm (S110): (a) 16.3 cm/min for ID = 12.5 cm; (b) 12.3 cm/min for ID = 14.4 cm

TABLE 2 Proposed Column Designs for the Plant-scale Process: 240 L of 0.0045-mM Mo and 0.0055-mM Competing Ions in 145-g-U/L Uranyl Nitrate and 0.1-M Nitric Acid Solution at 60°C (loading time = 2 hours; flow rate = 2.0 L/min, up-flow)^a

ID			Plant Designs with min. L_{plant}							1-M Stripping (down flow) for 99% Mo Recovery ^c				
			L_{min} (cm) ^b	Min. L_{plant} ^b (cm)	ΔP (atm)	CV (L)	$W_{sorbent}$ (kg)	Solution	u_s (cm/min)	Vol. (L)	Vol. (CV)	Time (min)		
(cm)	(in.)	Sorbent	d_p (μm)	L_{max} (cm) ^b										
12.5	4.9	S40	40	3.4	2.3	4.6	1.1	0.28	0.36	NH ₄ OH	16.3	1.9	3.4	2.0
12.5	4.9	S80	80	13.7	4.5	9.0	0.5	0.55	0.71	NH ₄ OH	16.3	4.7	4.2	4.8
12.5	4.9	S110	110	25.8	6.4	12.9	0.4	0.79	1.03	NH ₄ OH	16.3	7.3	4.6	7.6
14.4	5.7	S40	40	4.6	1.7	3.5	0.6	0.28	0.37	NH ₄ OH	12.3	2.1	3.8	1.7
14.4	5.7	S80	80	18.2	3.4	6.8	0.3	0.56	0.72	NH ₄ OH	12.3	5.3	4.8	4.2
14.4	5.7	S110	110	34.3	4.9	9.8	0.2	0.80	1.04	NH ₄ OH	12.3	8.5	5.3	6.6

^a Shaded text indicates that $\Delta P > 0.8$ atm.

^b At a given velocity, L_{max} is the column length when pressure drop during loading = 0.8 atm; L_{min} is column length from column inlet to the leading edge of 0.1% $C_{f,Mo}$. The minimum L_{plant} has a safety factor of 2: a capture column with $L_{0.1\%C_{f,Mo}}$ and a guard column with $L_{0.1\%C_{f,Mo}}$.

^c The stripping step starts from pH step change and ends until 99% Mo is recovered.

5 DOWN-SCALE COLUMN EXPERIMENTS

Results for down-scale column experiments for S40 and S110 are shown in Table 3. The feed solution contained 0.0045-mM stable Mo and tracer Mo-99 and 145-g-U/L uranyl nitrate. Linear velocities ranged from 3 to 9 cm/min, but results do not show an effect of linear velocity on Mo recovery. A significant amount of Mo is observed in the effluent at linear velocities of 5 and 9 cm/min (16–32%) for S40. This suggests that S40 would not be the best replacement for S110, despite the fact that VERSE predicted smaller column designs for S40. About 1–2% Mo is found in the effluent using S110, and recoveries vary from 73–89 ± 5% using 30 column volumes (CVs) of 1-M NH₄OH. Better temperature control of the feed solution (60–80°C) is expected to improve Mo adsorption on titania. Potassium permanganate was added to the water washes to ensure Mo was present as Mo(VI) for the runs performed on October 6, 2011, and October 12, 2011. Mo recovery results do not improve under these conditions when an oxidizing agent such as KMnO₄ is added.

TABLE 3 Results for Direct Down-scale Column Experiments for S110 and S40

Date of Run	Column Size (ID × L)	Velocity (cm/min)	Sorbent	%Mo in Effluent	%Mo in Washes	%Mo Recovered	Stripping Agent
09/15/11	1.5 × 3.1	9	S40	16.0	0.6	86.0	1 M NH ₄ OH
09/21/11	1.5 × 6.2	3	S110	1.0	0.6	88.0	1 M NH ₄ OH
09/23/11	1.5 × 6.3	5	S110	1.0	1.0	85.0	1 M NH ₄ OH
09/26/11	1.5 × 2.6	5	S40	32.0	0.3	80.0	1 M NH ₄ OH
09/28/11	1.5 × 6.3	10	S110	1.0	0.1	77.0	1 M NH ₄ OH
09/30/11	1.5 × 6.3	7.5	S110	2.0	0.1	85.0	1 M NH ₄ OH
10/06/11	1.5 × 6.2	7.5	S110	7.3	0.8	73.0 ^a	1 M NH ₄ OH
10/12/11	1.5 × 6.2	3	S110	7.0	1.0	89.0 ^a	1 M NH ₄ OH

^a 0.5 wt.% KMnO₄ added to first water wash for these runs.

6 CONCLUSIONS

Final column designs for the BWTSG plant-scale operation and mini-MIPS will utilize S110 sorbent with 60-Å pores. VERSE column designs suggest that S40 is the best replacement for S80, but experimental results show that S110 outperforms S40. The final column design for mini-MIPS is a 2.0-cm ID $\times$ 9.8-cm L column where 5 L of solution will pass through the column at a linear velocity of 12.3 cm/min. The final plant-scale column design is a 14.4-cm ID $\times$ 9.8-cm L column where 240 L of solution will pass through the column at a linear velocity of 12.3 cm/min. Results from mini-MIPS should tell us if an oxidizing agent such as KMnO_4 is needed to ensure Mo(VI) is not reduced upon irradiation.

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