Mo-99 Stripping Results and Column Designs for Mini-Medical Isotope Production System (MIPS)

Chemical Science and Engineering Division

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by

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Mo-99 STRIPPING RESULTS AND COLUMN DESIGNS FOR MINI-MEDICAL ISOTOPE PRODUCTION SYSTEM (MIPS)

1 INTRODUCTION

Results from the column tests performed by using small volumes of irradiated solutions as tracers for depleted uranium (DU) solutions containing stable molybdenum (Mo) as Na_2MoO_4 forced us to investigate the stripping parameters needed to obtain full Mo recovery. In an effort to optimize the stripping conditions, several column runs were done by using either 1 M NaOH or NH_4OH as the stripping agent at different velocities. Overall, we obtained very inconsistent results that suggest stripping velocity does not affect Mo recovery as much as originally believed. In addition, we generated 0.1 M HNO_3 breakthrough curves after each run to determine if the performance of the column was changing. Future experiments will utilize columns packed with fresh sorbent after each run.

The column designs for the mini-MIPS 5-liter (L) and 20-L experiments employed data obtained from using several different S80 columns at different loading, washing, and stripping velocities. Data were input into the VERSE code, and plant-scale column designs were generated. The mini-MIPS column designs and parameters are a direct downscale of the plant operation, where full Mo adsorption and recovery are expected.

2 EXPERIMENT

All column runs were performed on an AKTA liquid chromatography system (Figure 1). The feed solution contained DU as uranyl nitrate (~ 145 grams of uranium per liter [g-U/L]), stable Mo (0.0045 to 0.01 mM), and tracer Mo-99. Each column was equilibrated with 0.1 M HNO_3 prior to the feed solution being loaded onto the column. After the feed solution was loaded, the columns were washed with 10 column volumes (CVs) of 0.1 M HNO_3 and 10 CVs of H_2O . Mo was eluted from the column by using 30 CVs of base (1 M NaOH or NH_4OH). Finally, the columns were washed with 10 CVs of H_2O .

FIGURE 1 AKTA Liquid Chromatography Used for All Column Runs

3 STRIPPING EXPERIMENTS

Several different stripping experiments using 1 M and 1 M NaOH were performed in an effort to optimize conditions for full Mo recovery. Three different S80 columns were tested: (1) 1.5 cm inner diameter (*ID*) $\times$ 6.3 cm length (*L*) (stripping results obtained with 1 M NH_4OH), (2) 1 cm *ID* $\times$ 12.4 cm *L* (stripping results obtained with 1 M NaOH), and (3) 1.5 cm *ID* $\times$ 12.1 cm *L* (stripping results obtained with 1 M NH_4OH). Stripping experiments done with Column 2 used feed solutions that contained 0.01 mM Mo to compensate for other fission products that might adsorb on S80. Both Columns 2 and 3 were tested as potential candidates for the mini-MIPS 5-L experiment. However, inconsistent Mo recoveries forced us to question the performance of the S80 columns after multiple uses. Before and after each use of the 1.5 cm $\times$ 12.1 cm *L* S80 column, 0.1 M HNO_3 breakthrough curves were generated by using an in-line conductivity sensor as a means to examine when breakthrough had occurred. The conductivity measurements obtained suggest that the column performance is changing; however, when we looked at the pH of the solution when breakthrough had occurred, results were similar. For example, the initial breakthrough of 0.1 M HNO_3 on Column 3 occurred when the pH reached 1.65. After a single run, breakthrough occurred when the pH reached 1.5; after two runs, it occurred when the pH reached 1.57; and finally, after a third run, breakthrough was not reached after 100 mL of 0.1 M HNO_3 passed through the column, but the final pH did not go below 1.67. These results can be seen in Figure 2.

FIGURE 2 Plot of 0.1 M HNO_3 Curves after Each Column Run (1.5 cm *ID* $\times$ 12.1 cm *L* S80)

The results from the stripping experiments are shown in Table 1. Mo recovery as a function of stripping velocity is variable, and no single velocity always yields full recovery. However, a more thorough investigation of column performance as a function of the number of uses is underway. The results from the column runs using a potential mini-MIPS column have shown that a loading velocity of 15 cm/min or less is needed to ensure that 1% or less Mo is found in the effluent. In addition, the stripping velocity for mini-MIPS is currently set at 10 cm/min. Mo recoveries much greater than 100% are highlighted in yellow in Table 1.

The main reason for the large recoveries is the fact that Mo was still adsorbed on the column after the same S80 column was used multiple times without obtaining full recovery. The 294% recovery obtained on March 24, 2011, is questionable, and a large pipetting or counting error in the feed or strip solution with the most activity is a possible explanation. A column with a larger *ID* is needed for mini-MIPS to ensure full Mo adsorption. The current designs for the mini-MIPS 5-L column run are a 2.0 cm *ID* $\times$ 10 cm *L* S80 column (load of 4,637 mL at 12.3 cm/min) or a 2.1 cm *ID* $\times$ 10 cm *L* S80 column (load of 5,112 mL at 12.3 cm/min). The current design for the 10- to 20-L mini-MIPS experiment is a 2.5–2.9 cm *ID* $\times$ 10 cm *L* column. These column sizes are direct downscales of the MIPS plant-scale column design, which is currently set to be a 14.4 cm *ID* $\times$ 10 cm *L* S80 column for passing 240 L of solution through the column in roughly 2 hours.

TABLE 1 S80 Laboratory-Scale MIPS Experimental Results, Stripping = 1 M NaOH (down flow), 60°C, Feed = Mo and ~145 gU/L Uranyl Nitrate, pH = 1 (up flow)

Parameters	Experiment Date												
	3/18	3/23	3/24	3/30	4/1	4/7	3/24	3/28	4/4	4/13	3/17	3/16	3/14
File name	21	21-10a	21-10b	15-10a	15-10b	15-10c	15-5a	15-5b	15-5c	15-5d	21-10	15-7.5	15-5
L (cm) ^a	6.3	6.3	6.3	12.4	12.4	12.4	6.3	6.3	12.4	12.4	12.4	12.4	12.4
ID (cm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.0	1.0	1.0
Loading (up flow)													
$C_{f(Mo)}$ (mM)	0.0045	0.0045	0.0045	0.0045	0.0045	0.0045	0.0045	0.0045	0.0045	0.0045	0.01	0.01	0.01
V_{feed} (mL)	4452	4452	4452	5000	5000	4075	3180	3180	5000	5000	1980	1323	1222
V_{feed} (CV)	400	400	400	228	228	191	286	286	228	228	90	60	56
F (mL/min)	37.1	37.1	37.1	26.5	26.5	26.5	26.5	26.5	26.5	26.5	16.5	11.8	11.8
u_s (cm/min)	21	21	21	15	15	15	15	15	15	15	21	15	15
Time (min)	120	120	120	189	189	120	120	120	189	189	120	112	104
Stripping (down flow)													
$V_{stripping}$ (mL)	326	326	326	651	745	651	326	326	651	651	320	293	293
$V_{stripping}$ (CV)	29	29	29	30	34	30	29	29	30	30	15	13	13
F (mL/min)	37.1	17.7	17.7	17.7	17.7	17.7	8.8	8.8	8.8	8.8	17.7	13.3	8.8
u_s (cm/min)	21	10	10	10	10	10	5	5	5	5	10	7.5	5
Time (min)	9	19	19	37	42	37	37	37	74	74	7.9	5.9	3.9
Sample Size (mL)	23.3	23.3	23.3	46.5	10, 25	10	23.3	23.3	10	10	20.9	20.9	20.9
pH curve ^b	Y	Y	Y	Y	Y	N	Y	Y	Y	Y	N	N	N
% Mo													
Flow-through	1	2	3	2	16	6	4	2	9	7	0	0	0
Recovered	57	54	165 ^c	88	59	104	294 ^c	39	71	60	77	91	156 ^c

^a 1 CV was 11.1 mL for $L = 6.3$ cm and was 21.9 mL for $L = 12.4$ cm. The effluent was collected at the ultraviolet (UV) detector outlet and sent to y counter ($\pm 5\%$). DV_{system} from the injection valve to the UV detector was 1.95 mL. $DV_{cap} + DV_{system}$ was 2.90 mL (0.3 CV) for $L = 6.3$ cm and was 2.62 mL (0.1 CV) for $L = 12.4$ cm.

^b Experiments with pH curves during stripping are listed as Y; experiments without pH data are listed as N.

^c Mo recoveries much greater than 100%.

4 ESTIMATION AND VERIFICATION OF SOLVENT-MODULATED ISOTHERM PARAMETER(S) FOR NaOH

In the NaOH stripping experiments, the stripping effluent was collected in fractions, and samples were gamma counted (Table 1). A solvent-modulated isotherm parameter (S) for NaOH was estimated by comparing the experimental Mo stripping curves with VERSE simulations. The S value was estimated from experiments with small sample fractions (10 mL, Figure 3) and was further tested for experiments with large sample fractions (> 20 mL, Figures 4 and 5).

VERSE simulations obtained $100\% \pm 0.5\%$ of Mo recovery with the reported numerical parameters (Tables 2–5). However, Mo recovery in the actual experiments varied from 39% to 294% (Table 1). To describe the experimental stripping curves, the loading flow rates in simulations were adjusted such that the amount of Mo recovered in the simulations and in the experiments was identical. The simulated loading flow rate was calculated by the following equation: simulated loading flow rate = feed volume $\times$ Mo recovery/loading time. Other operating parameters—such as column dimensions, loading time, stripping flow rates, and stripping time—were the same as those used in the experiments. Simulations with 100% experimental Mo recovery were also plotted for comparison (Figures 3, 4, and 5).

After 1 M NaOH entered the column inlet, experimental pH curves showed that about 0.5 CV of stripping solution was needed to change the effluent pH. However, an immediate pH step change at the stripping step was simulated in VERSE simulations. To account for the 0.5 CV pH step change in the experiments, simulations were plotted with an additional 0.5 CV of elution volume (Figures 3, 4, and 5).

To estimate the range of S , the contribution of dead volume was simulated as plug flow in nature or dispersion in two continuously stirred tank reactors (CSTRs). The minimum S was estimated by assuming no dispersion in the dead volume. The maximum S was estimated by assuming that the dispersion in the dead volume was two CSTRs, with one CSTR being before the column and another being after the column. Under both conditions, the S of NaOH on S80 was estimated to be 7 (Figure 3).

Simulations with the same set of isotherm, mass transfer, and numerical parameters were further tested and compared with stripping data from experiments with large sample sizes (Figures 4 and 5). Simulations agreed closely with experimental peak positions and peak areas. Peak shapes in simulations and experiments were expected to agree, if small sample sizes were collected in the experiments.

TABLE 2 Intrinsic Model Parameters Tested in VERSE (uranyl nitrate at pH 1, 60°C)

Sorbent	System Parameters					
	$P_{dry\ packing}$ (g/mL)	d_p Range (μm)	$d_{p,avg}$ (μm)	Pore Size ($\text{\AA}$)	b (–)	p (–)
S80	1.3	80	80	60	0.33	0.66
T52	1.5	200–400	300	100	0.30	0.66
T5M	1.1	200–400	300	100	0.34	0.71
Al_2O_3	1.1	50–200	125	60	0.35	0.63

TABLE 3 Modulated Langmuir Isotherm Parameters for Mo in 145 g-U/L $\text{UO}_2(\text{NO}_3)_2$ at pH 1

Sorbent	Estimated from Batch Tests			Estimated from Frontal Data			
	a (–)	b (1/mM)	$q_{max} = a/b$ (mM)	b (1/mM)	$q_{max} = a/b$ (mM)	S for NaOH (–)	S for NH4OH (–)
S80	5,479	34	161	80	68	7	7–9
T52	13,127	56	233	-	-	10–30	5
T5M	4,697	36	130	70	67	10–30	1
Al_2O_3	109	23	5	12	9	No data	3

TABLE 4 Mass Transfer Parameters

Solution	pH 1 Solution		pH 14 Solution		$D_{(x)}/D_p$
	Mo in Uranyl Nitrate	U in HNO_3	NaOH in Water	NH_4OH in Water	
$D_{(x)}$ (cm^2/min)	1.1×10^{-3}	9.9×10^{-4}	1.7×10^{-3}	2.5×10^{-3}	
D_p (cm^2/min) ^a					
S80	4.4×10^{-5}	4.0×10^{-5}	6.8×10^{-5}	1.0×10^{-4}	25
T52	3.0×10^{-5}	2.7×10^{-5}	4.6×10^{-5}	6.8×10^{-5}	37
T5M	1.0×10^{-4}	9.0×10^{-5}	1.6×10^{-4}	2.3×10^{-4}	11
Al_2O_3	7.3×10^{-6}	6.6×10^{-5}	1.1×10^{-5}	1.7×10^{-5}	150
Eb (cm^2/min)	Chung and Wen correlation ^b				
kf (cm/min)	Wilson and Geankopolis correlation ^c				

^a D_p was estimated from the respective Mo breakthrough curve in uranyl nitrate at pH 1. For Mo feed solution at 60°C: viscosity = 0.74 cP, density = 1.28 g/mL. For stripping solution at 60°C: viscosity = 0.47 cP, density = 0.98 g/mL.

^b Source: Chung and Wen (1968).

^c Source: Wilson and Geankopolis (1966).

TABLE 5 Numerical Parameters

No. of Axial Elements	Max. Step Size (A_{0max}) (CV)	Collocation Points		Tolerance		
				Absolute (mM)		Relative
		Axial	Particle	Mo	Uranyl Nitrate, NaOH, NH_4OH	
100	0.1	4	4	5.0×10^{-8}	10^{-3}	10^{-3}

(a) 15-10b (Mo recovery = 59%)

(b) 15-10c (Mo recovery = 104%, no pH data)

(c) 15-5c (Mo recovery = 71%)

(d) 15-5d (Mo recovery = 60%)

FIGURE 3 Estimation of S for NaOH from Stripping Curves with 10-mL Sample Size and Mo of 0.0045 mM (The pH curves were plotted to show the pH step change at the effluent. The black dashed lines were simulations assuming experiments reached 100% Mo recovery from the experimental loading conditions. More experimental details can be found in Table 1.)

(a) 21 (Mo recovery = 57%)

(d) 15-10a (Mo recovery = 88%)

(b) 21-10a (Mo recovery = 54%)

(e) 15-5a (Mo recovery = 294%)

(c) 21-10b (Mo recovery = 165%)

(f) 15-5b (Mo recovery = 39%)

FIGURE 4 Verification of S for NaOH from Stripping Curves with >20 -mL Sample Size and $Mo = 0.0045$ mM (The pH curves were plotted to show the pH step change at the effluent. The black dashed lines were simulations assuming experiments reached 100% Mo recovery from the experimental loading conditions. More experimental details can be found in Table 1.)

(a) 21-10 (Mo recovery = 77%)

(b) 15-7.5 (Mo recovery = 91%)

(c) 15-5 (Mo recovery = 156%)

FIGURE 5 Verification of S for NaOH from Stripping Curves with >20 mL Sample Size and Mo of 0.01 mM (The black dashed lines were simulations assuming experiments reached 100% Mo recovery from the experimental loading conditions. More experimental details can be found in Table 1. No pH data shown.)

5 COMPARISON OF VERSE SIMULATIONS WITH EXPERIMENTAL NH₄OH STRIPPING RESULTS

The solvent-modulated isotherm parameter (S) for NH₄OH was estimated, verified, and reported in Part 3 of the December 2010 progress report (Chung et al. 2010). Simulations were tested and compared with experimental stripping curves at stripping velocities of 5, 10, and 21 cm/min by using 1 M NH₄OH (Figure 6). Details about loading and stripping conditions are summarized in Table 6. Simulation peak positions and peak areas agreed closely with those in Experiments 21-5 and 21-10b. The peak-area disagreement in Experiments 21 and 21-10a was unclear. The peak shapes in simulations and experiments were expected to agree, if small sample sizes were collected in experiments.

The contribution of dead volume affected the S values. The S values for NH₄OH ranged between 7 (plug flow) and 9 (CSTR). A small S results in a short peak with a long tail, whereas a large S results in a tall peak with a short tail (Figure 6). Previous experimental data showed that the dead volume from the AKTA unit at Argonne was plug flow in nature (Chung et al. 2010). Simulations with dispersion in two CSTRs are shown for comparison.

TABLE 6 S80 Laboratory-Scale MIPS Experimental Results, Stripping = 1 M NH₄OH (down flow); 60°C, Feed = Mo and ~145 g-U/L Uranyl Nitrate, pH = 1 (up flow)

Parameter	File Name			
	21	21-10a	21-5	21-10b
L (cm) ^a	6.3	6.3	6.3	12.3
ID (cm)	1.5	1.5	1.5	1.0
Loading (up flow)				
$C_{f(Mo)}$ (mM)	0.01	0.0061	0.0063	0.0045
V_{feed} (mL)	4454	4454	4454	1980
V_{feed} (CV)	400	400	400	208
F (mL/min)	37.1	37.1	37.1	16.5
u_s (cm/min)	21	21	21	21
Time (min)	120	120	120	120
Stripping (down flow)				
$V_{stripping}$ (mL)	504	504	504	320
$V_{stripping}$ (CV)	45	45	45	34
F (mL/min)	37.1	17.7	8.8	7.9
u_s (cm/min)	21	10	5	10
Time (min)	14	28.5	57	41
Sample size (mL)	36	36	36	20.9
pH curve ^b	N	N	N	N
% Mo				
Flow-through	1	1.4	0.2	7
Recovered	69	105	92	77

^a 1 CV was 11.1 mL for $L = 6.3$ cm and 9.7 mL for $L = 12.3$ cm. The effluent was collected at the UV detector outlet and sent to y counter ($\pm 5\%$). DV_{system} from the injection valve to the UV detector was 1.95 mL. $DV_{cap} + DV_{system}$ was 2.90 mL (0.3 CV) for $L = 6.3$ cm and 2.62 mL (0.1 CV) for $L = 12.3$ cm.

^b Experiments with pH curves during stripping are listed as Y; experiments without pH data are listed as N.

FIGURE 6 Verification of S for NH_4OH from Stripping Curves with >20-mL Sample Size (The black dashed lines were simulations assuming experiments reached 100% Mo recovery from the experimental loading conditions. More experimental details can be found in Table 6. No pH data shown.)

6 MIPS PLANT COLUMN DESIGNS

MIPS plant columns were designed based on VERSE simulations. System, isotherm, mass transfer, and numerical parameters tested in VERSE simulations are listed in Tables 2–5. In the designs, the feed solution consisted of 0.0045 mM Mo, 0.0055 mM of other competing ions, 0.1M HNO₃, and 145 g-U/L uranyl nitrate at 60°C. A feed volume of 240 L was loaded onto the column in the up-flow direction in 2 hours. The loading flow rate was fixed at 2 L/min (= 240 L/120 min).

To maintain a constant loading flow rate, velocities were decreased for columns with a large *ID*, while velocities were increased for small-*ID* columns. For MIPS plant columns, the *ID* ranged between 11.0 and 14.4 cm for S80 (Tables 7 and 8). The maximum *ID* was 14.4 cm because the pipe size for production was limited to 14.4 cm. The minimum *ID* of 11.0 cm was constrained by the maximum pressure drop of 0.8 atm. The range of *ID* decided the range of superficial velocity during loading ($u_{s,loading}$), at a given flow rate. Therefore, $u_{s,loading}$ ranged between 12.3 and 21.0 cm/min for MIPS plant columns using S80. The $u_{s,loading}$ tested below included 12.3, 13.0, 15.8, 16.3, 17.7, and 21.0 cm/min.

The minimum column length (L_{min}) was then estimated at each $u_{s,loading}$. L_{min} was the column length from column inlet to 0.1% of Mo concentration in the feed (0.1% $C_{f, Mo}$). To ensure full Mo capture during loading, the length of the plant column was designed as 2 L_{min} . The additional L_{min} in the plant column will serve as a guard column to prevent Mo loss. When $u_{s,loading}$ was <21.0 cm/min, or when *ID* was >11.0 cm, 2 L_{min} < L_{max} , where L_{max} was the column length when the pressure drop reached 0.8 atm during loading at a given velocity. When $u_{s,loading}$ = 21.0 cm/min, the pressure drop can be reduced by using a column with a length of <2 L_{min} . However, a column with a column length of <2 L_{min} could lead to possible Mo loss.

Stripping conditions using either NaOH or NH₄OH were tested in simulations (Figures 7 and 8). The flow direction during stripping was down flow. The velocity during stripping was fixed at 10 cm/min because high Mo recovery could be achieved at this velocity in most experiments. The amount of NH₄OH for Mo recovery was calculated based on simulations with no dispersion in the dead volume (plug flow), because the AKTA unit at Argonne was plug flow in nature. When the contribution of dead volume was plug flow in nature, the *S* value was 7 for NaOH and NH₄OH. The difference between NaOH and NH₄OH in simulations was in the mass transfer parameters, which affected the spreading of the peak.

The stripping conditions for 95% and 99% Mo recovery are listed in Tables 7 and 8, respectively. About 95% of the Mo was recovered in the first three CVs (less than 4 L) of stripping, or within 4 minutes. About 99% of the Mo was recovered in the first five CVs (less than 6 L) of stripping, or within 6 minutes. However, during stripping, peak tailing was observed in both experimental and simulated Mo peaks. A long stripping time or more stripping solution would be required to increase Mo recovery.

TABLE 7 Proposed S80 Column Designs for Plant Operation for 95% Mo Recovery^a

<i>ID</i> ^b		Plant Designs with Minimum L_{plant} ^d								1M Stripping (down flow) for 95% Mo Recovery ^e				
		$u_{s, loading}$ (cm/min)	L_{max} (cm) ^c	L_{min} (cm) ^c	Minimum L_{plant} (cm)	ΔP (atm)	CV (L)	$W_{sorbent}$ (kg)	Sorbent Cost (\$)	Solution	u_s (cm/min)	Vol. (L)	Vol. (CV)	Time (min)
14.4	5.7	12.3	18.2	3.4	6.8	0.30	0.56	0.72	869	NH ₄ OH	10	3.7	3.3	2.9
14.0	5.5	13.0	17.2	3.6	7.2	0.34	0.55	0.72	866	NH ₄ OH	10	3.6	3.2	3.0
12.7	5.0	15.8	14.1	4.3	8.7	0.49	0.55	0.72	859	NH ₄ OH	10	3.3	3.0	3.3
12.5	4.9	16.3	13.7	4.5	9.0	0.52	0.55	0.71	858	NH ₄ OH	10	3.3	3.0	3.4
12.0	4.7	17.7	12.6	4.8	9.7	0.62	0.55	0.71	855	NH ₄ OH	10	3.2	2.9	3.6
11.0	4.3	21.0	10.6	5.7	11.5	0.87	0.54	0.71	850	NH ₄ OH	10	3.0	2.8	4.0
14.4	5.7	12.3	18.2	3.4	6.8	0.30	0.56	0.72	869	NaOH	10	3.8	3.5	3.0
14.0	5.5	13.0	17.2	3.6	7.2	0.34	0.55	0.72	866	NaOH	10	3.6	3.3	3.0
12.7	5.0	15.8	14.1	4.3	8.7	0.49	0.55	0.72	859	NaOH	10	3.4	3.0	3.4
12.5	4.9	16.3	13.7	4.5	9.0	0.52	0.55	0.71	858	NaOH	10	3.3	3.0	3.4
12.0	4.7	17.7	12.6	4.8	9.7	0.62	0.55	0.71	855	NaOH	10	3.2	2.9	3.6
11.0	4.3	21.0	10.6	5.7	11.5	0.87	0.54	0.71	850	NaOH	10	3.0	2.8	4.1

^a 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 at 60°C; loading time = 2 hours; flow rate = 2.0 L/min (up flow); $DV = 4\%$ CV . The minimum L_{plant} has a safety factor of 2; a capture column with length $L = 0.1\% C_{f(Mo)}$; and a guard column with $L = 0.1\% C_{f(Mo)}$.

^b According to S. Aase (engineer, Babcock and Wilcox Technical Services Group), the column ID has to be no greater than the pipe size; it must be less than 14.4 cm or 5.7 in.

^c At a given velocity, L_{max} is the column length when the pressure drop during loading = 0.8 atm; L_{min} is the column length from the column inlet to the leading edge of $0.1\% C_{f(Mo)}$.

^d Feed volume is about 420–440 CV.

^e The stripping step starts from the pH step change and ends when 95% Mo is recovered.

TABLE 8 Proposed S80 Column Designs for Plant Operation for 99% Mo Recovery^a

<i>ID</i> ^b		Plant Designs with Minimum L_{plant} ^d								1 M Stripping (down flow) for 99% Mo Recovery ^e				
		$u_{s, loading}$ (cm/min)	L_{max} (cm) ^c	L_{min} (cm) ^c	Minimum L_{plant} (cm)	ΔP (atm)	CV (L)	$W_{sorbent}$ (kg)	Sorbent Cost (\$)	Solution	u_s (cm/min)	Vol. (L)	Vol. (CV)	Time (min)
14.4	5.7	12.3	18.2	3.4	6.8	0.30	0.56	0.72	869	NH ₄ OH	10	5.3	4.8	4.2
14.0	5.5	13.0	17.2	3.6	7.2	0.34	0.55	0.72	866	NH ₄ OH	10	5.2	4.7	4.3
12.7	5.0	15.8	14.1	4.3	8.7	0.49	0.55	0.72	859	NH ₄ OH	10	4.7	4.3	4.7
12.5	4.9	16.3	13.7	4.5	9.0	0.52	0.55	0.71	858	NH ₄ OH	10	4.7	4.2	4.8
12.0	4.7	17.7	12.6	4.8	9.7	0.62	0.55	0.71	855	NH ₄ OH	10	4.5	4.1	5.0
11.0	4.3	21.0	10.6	5.7	11.5	0.87	0.54	0.71	850	NH ₄ OH	10	4.2	3.8	5.6
14.4	5.7	12.3	18.2	3.4	6.8	0.30	0.56	0.72	869	NaOH	10	5.5	5.0	4.3
14.0	5.5	13.0	17.2	3.6	7.2	0.34	0.55	0.72	866	NaOH	10	5.2	4.7	4.3
12.7	5.0	15.8	14.1	4.3	8.7	0.49	0.55	0.72	859	NaOH	10	4.8	4.3	4.8
12.5	4.9	16.3	13.7	4.5	9.0	0.52	0.55	0.71	858	NaOH	10	4.7	4.2	4.9
12.0	4.7	17.7	12.6	4.8	9.7	0.62	0.55	0.71	855	NaOH	10	4.5	4.1	5.1
11.0	4.3	21.0	10.6	5.7	11.5	0.87	0.54	0.71	850	NaOH	10	4.2	3.8	5.6

^a 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 at 60°C; loading time = 2 hours; flow rate = 2.0 L/min (up flow); $DV = 4\%$ CV. The minimum L_{plant} has a safety factor of 2; a capture column with length $L = 0.1\% C_{f(Mo)}$; and a guard column with $L = 0.1\% C_{f(Mo)}$.

^b According to S. Aase (engineer, Babcock and Wilcox Technical Services Group), the column ID has to be no greater than the pipe size; it must be less than 14.4 cm or 5.7 in.

^c At a given velocity, L_{max} is the column length when the pressure drop during loading = 0.8 atm; L_{min} is the column length from the column inlet to the leading edge of $0.1\% Cf(Mo)$.

^d Feed volume is about 420–440 CV.

^e The stripping step starts from the pH step change and ends when 95% Mo is recovered.

Figure 7 Stripping Results for MIPS S80 Plant Columns Using 1 M NH_4OH (More information about simulations can be found in Tables 7 and 8. The stripping volume was calculated from the plug flow simulations.)

FIGURE 8 Stripping Results for MIPS S80 Plant Columns Using 1 M NaOH (More information about simulations can be found in Tables 7 and 8.)

7 MINI-MIPS

Argonne has developed a concept to use the linac accelerator to provide a mini-MIPS demonstration. We are considering a two-stage approach. In the first stage, a 20-MeV linac will be used to irradiate a 5-L uranyl nitrate solution containing 150-g/L of LEU with neutrons from a tantalum target; the maximum solution power will be ≤ 0.05 kW/L. At least two full-scale irradiations will be performed. After irradiation, a small aliquot will be taken to perform batch K_d measurements, but the bulk of the solution will be run through a Mo recovery column. (This will allow a direct comparison between batch and column studies.) These results should help us better understand what other fission products in addition to Zr-95, Te-132, I-131, and Mo-99 are adsorbing on S80 and where they end up after being contacted with nitric acid, water, and ammonium hydroxide. The samples from the Armed Forces Radiobiology Research Institute (AFRRI) showed us some of the fission products that will adsorb on S80, but they did not confidently tell us whether they are washed off or remain adsorbed on S80 because the errors associated with those results were high.

In the second stage, the linac, now a 58-MeV machine, will irradiate a DU target for use with a 10- to 20-L solution (same composition as Stage 1); the maximum solution power will be ≤ 0.5 kW/L. We will then, with the assistance of B&W, attempt to make the mini-MIPS as applicable to the actual MIPS operation as possible, while still obtaining data that are vital to the design of the MIPS. The tantalum or DU target and the solution will be contained in a shielded cell. A glovebox will be connected to the shielded cell. Off-gases from all sources will be contained in a pressurized tank to allow the storage decay of radioactive fission gases. A catalytic convertor and a condenser will be built into the mini-MIPS off-gas loop to return water to the solution. A system to meter concentrated nitric acid into the condensed water stream for return to the fuel solution will also be in place, as will a system to add additional water to the fuel solution, if required.

Gas analysis will be performed above the fuel solution by using a separate sampling loop. We will also have the ability to monitor the off-gas after it passes through the H_2/O_2 -recombiner/condenser operation. The system will allow on-line monitoring of off-gas generation (rate and composition).

A fuel solution sampling loop will allow timed sampling of the solution during operation. During irradiation, an in-line pH probe will be used for measuring fuel-solution pH, and an in-line density or conductivity device will be used to monitor water loss from the fuel solution during operation. This will give us some insight into how pH changes as a function of irradiation time and most likely a good indication of how much and how often nitric acid will need to be added to the fuel solution to maintain a pH of 1.0 ± 0.3 .

The shielded cell will also contain a Mo recovery column for removing and concentrating Mo from the fuel solution after irradiation. The Mo-product solution will be pumped to the glovebox during column elution. The product solution will then be removed from the glovebox for further purification in one of our radiochemistry laboratories. All effluents will be sampled

during the Mo recovery operation by using an automatic syringe system installed in the glovebox.

In Stage 1, up to 2.3 Ci of Mo can be produced in a 50-hour end of irradiation. The total concentration of all Mo isotopes expected from the 5-L mini-MIPS experiment is approximately 4.2×10^{-5} mM; as a result, before irradiation, stable Mo will be added to the feed solution to match the concentration of Mo expected in MIPS, which is 0.0045 mM. The column sizes have been designed for a Mo concentration of 0.0045 mM. After recovery from the solution, the Mo-99 can be purified by using the LEU-modified Cintichem process,¹ and the resultant Mo-99 product can be shipped to Covidien for testing.

The following data-collection objectives are planned for mini-MIPS Stage 1:

- We will collect on-line off-gas compositional and generation rates over time. Gas samples will be analyzed from the start of operation, throughout the “march” to steady state, and during steady-state operation by using a gas chromatograph (GC) with a mass spectrometer (MS) and a thermal conductivity detector. The technique was developed for measuring gas samples from AFRRI-irradiated solutions. On-line operation will be optimized by using Van de Graaff irradiations of uranyl nitrate solutions.² This technique was developed for measuring H₂, O₂, N₂, and nitrogen oxide compounds. Other techniques will need to be developed for measuring iodine and noble-gas fission products. Ammonia may or may not be measurable by the GC system; this must be assessed. If we cannot detect ammonia with GC-MS, we may be able to detect the ammonium ion using ion chromatography. Ion chromatography will require the bulk of uranium to be removed from the sample and the sample to be distilled before it is analyzed. These measurements will aid in determining potential research and development needed in MIPS Stage 2 for off-gas handling.
- We will collect solution samples during the irradiation to measure changes in pH and potential water loss versus time of irradiation. We will also try inserting a pH probe in the sampling loop to measure pH in real time. An in-line solution density or conductivity probe will also be inserted in the fuel-solution sampling loop; either measurement will be useful in monitoring if the solution is being concentrated through loss of water during irradiation.
- The fuel-solution samples collected over time may also be useful for measuring other solution properties (e.g., iodine speciation and solution Redox potential, and concentrations of ammonium ion, nitrite, and peroxide). Samples

¹ Future experiments could also purify the Mo product by using the National Atomic Energy Commission Argentina (CNEA) process, but this will require additional development and coordination with CNEA to duplicate what will be performed in Argentina.

² Plans will also be developed for measuring iodine in the off-gas streams. This technique will need to be developed and verified before use.

will be collected by using an automatic syringe system in the glovebox during irradiation and will be collected and analyzed after irradiation is complete. Initial experiments will be run for short periods to allow Argonne to determine the flow rate of concentrated nitric acid into the solution required to maintain a pH of 1 ± 0.3 during the 50-hour “production” run. Even if use of the pH probe is not successful, because pH can be measured within 1 hour of the end of irradiation, the lag-time effect experienced with AFRRRI samples will be eliminated. Although it will take a longer time to measure other solution properties (I speciation, NH_4 and peroxide concentrations), the 3- to 10-day lag-time for shipping samples from AFRRRI will be eliminated. These samples can also be used as tracers to perform additional recovery-column and purification demonstration runs, thus allowing a better understanding of what went wrong during the September 2010 demonstrations and preparing us to perform a successful demonstration for the column purification run planned with the 5 L uranyl nitrate solution that will be irradiated for 50 hours.

- We will demonstrate the recovery and purification of Mo from the fuel solution at the Ci level and ship a sample to Covidien for testing. Assuming that (1) the recovery and purification system has been optimized from earlier experiments with doped DU solutions and (2) the product solution can arrive at Covidien within 3 days after the end of irradiation, Covidien should have 1 Ci of Mo-99 for testing.
- We will collect samples of all column effluent streams during column operation to establish the elution profile for each operation.

The stage-2 objectives follow will be to:

- Duplicate the objectives of Stage 1 but at significantly higher solution powers,
- Provide additional samples of product to Covidien, and
- Use the mini-MIPS as a test-bed for developing the MIPS design.

Since upcoming linac experiments call for a two-sided target irradiation, a beam port will enter the shielded cell on both sides. The projected inside dimensions of the glovebox are 40 in. wide by 38 in. high by 31 in. deep. It will have 8-in. lead shielding on the front face, with 4 in. on the other sides.

The GC-MS will be located behind a shield wall in the target room, as will the pH meter and instrumentation for the density and/or conductivity device.

During irradiation, the solution will be cooled by using a heat exchanger. A thermostated-bath circulator will be on a second valved line to heat the fuel solution and the Mo-recovery column during Mo extraction.

We envision using 1/16-in. outer diameter (*OD*) steel tubing for all liquid and gas transport. The only exception is the dump line between the target vessel and the dump tank, which will have a 1/4-in. *OD*, large enough to allow passage of the solution into the dump tank without the need of pressure or a vacuum draw. All valves and sampling syringes will be servo-operated, except the valve for direct transfer of the fuel solution from the target tank to the dump tank, which will be manually operated. All sampling loops will be located in glovebox.

The fuel solution will remain in the shielded cell, located in either the target tank or the dump tank below the shielded cell. All column effluents, except the Mo-depleted fuel solution, will flow to tanks in the glovebox.

Cold feeds to the Mo-recovery column operation, the concentrated nitric acid solution for pH stabilization, and the fuel-solution water make-up will be located outside containment.

Peristaltic pumps will be used for the gas and fuel-solution sampling loops. Fluid Metering Inc. (FMI) positive-displacement pumps will be used for passing feeds through the Mo-recovery column and for the fuel-solution water make-up line. A syringe pump will be used to meter concentrated nitric acid to the fuel solution during operation. Load cells will be placed under cold-feed tanks to the Mo-recovery column to monitor flow rates.

The fuel solution in the target tank will be temperature-controlled by using a heat exchanger cooled by once-through laboratory water. The temperature of the Mo-recovery column will be maintained by a thermostated jacket connected to a thermostated bath circulator. The fuel solution in the target tank will be heated through the same circulating system during column operation.

Thermocouples will be placed in the target tank and the solution-feed and solution-exit sides of the Mo-recovery column.

The off-gas pressure will be controlled by a two-pump, three-tank system. The tanks will be in series to allow the pressure in the mini-MIPS system to be controlled during linac irradiation, to collect off-gas from the tanks and column, and to move the fuel solution from the dump tank to the target tank. The first pump will be a low-power pump that will be used to control the pressure of the system. The second pump will draw gases from the second tank to store them at high pressure in a SCUBA tank. All gases from the experiment will be pressurized and stored for radioactive decay. A gas cylinder (He or N₂) will be connected to the system to bleed gas into the system as required.

We are planning to use LabView (Laboratory Virtual Instrumentation Engineering Workbench) to control valves, pumps, and sampling syringes and to collect data.

8 CONCLUSIONS AND FUTURE WORK

The stripping results are of concern because they are inconsistent and variable. Future column runs will use columns packed with unused sorbent to determine if better Mo recovery results can be obtained when fresh sorbent is used each time. A 2-cm $ID \times 10$ -cm L S80 column has been packed and will be tested under conditions predicted by VERSE for the 5-L mini-MIPS experiment. The results from runs using this column will be used to predict what type of results can be expected for the mini-MIPS 5-L experiment using a 2-cm $ID \times 10$ -cm L S80 column under optimum conditions.

9 REFERENCES

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