Documenting Dual-Column Experiment with Mini-SHINE Solution

Chemical Science and Engineering Division

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DOCUMENTING DUAL-COLUMN EXPERIMENT WITH MINI-SHINE SOLUTION

1 INTRODUCTION

Argonne National Laboratory (Argonne) is assisting SHINE Medical Technologies (SHINE) in developing a production method and recovery and purification processes for molybdenum 99 (Mo-99) using an accelerator-driven, subcritical target consisting of an aqueous uranyl-sulfate solution. An integral part of the process is the development of a column for the separation and recovery of Mo-99, followed by a concentration column to reduce the product volume from 15–25 L to <1 L prior to entry into the low-enriched uranium (LEU)-Modified Cintichem purification process. Argonne has developed plant-scale column designs for the initial Mo-recovery column and the concentration column.

Equipment for the Mo recovery and concentration column has been set up in the Argonne linac facility as part of the mini-SHINE experiment. We completed a column experiment using a linac-irradiated, enriched-uranium-sulfate, micro-SHINE solution as a spike for a depleted uranium (DU) sulfate solution to collect preliminary data for the next stage of the mini-SHINE experiments.

2 Mo RECOVERY SETUP

Two gloveboxes were installed and set up during fiscal year 2013 (FY13) for the mini-SHINE project. The first, the target-solution-monitoring glovebox, is described in another report (Youker et al. 2013). The second is the remotely operated Mo-recovery glovebox. This section describes the activities completed in FY13 that led to the installation and testing of the two systems.

Figure 1 is a flow diagram of the Mo-recovery process. Implementation of the flow diagram in the Mo-recovery glovebox is shown in Figure 2. A positive-displacement pump serves the Mo-recovery glovebox and is shared with the target-solution-monitoring glovebox. During Mo recovery, the positive-displacement pump draws the irradiated mini-SHINE target solution from the target vessel. The solution enters the Mo-recovery glovebox through one of the inlet solenoid valves on the left side. The target solution containing the full complement of fission and activation products is then fed onto the heated recovery column from the bottom. The solution is heated to 80°C in the lower pre-heater before being introduced onto the column. The column effluent passes through one of the 16-loop trapping flowpath selector (TFS) sampling valves before passing through the pump. After passing through the column, the target solution exits the Mo-recovery glovebox through one of the outlet solenoid valves on the right side as it is directed to the target-solution dump tank that sits beneath the mini-hot cell. After washing the column with a sulfuric acid solution and then water, the Mo-99 is stripped from the column using 0.1 M sodium hydroxide (NaOH). During stripping, the solution is heated to 80°C in the upper pre-heater before passing through the heated column from the top. The solution then passes through one of the TFS sampling valves before passing through the pump as it is directed to the Mo-recovery cask that resides outside of the glovebox. Column-washing effluents are captured in plastic bottles that reside in the rear, right side of the glovebox; they are vented to the gas collection system. The wash solutions also pass through the TFS sampling valve, where timed samples are collected before being captured in plastic bottles.

Samples are retrieved from the TFS sampling valves using pre-evacuated vials that are sealed with a septum. The vacuum in the 10-mL vials have been shown to fully draw the solution samples. A miniature vacuum pump was installed in each glovebox. The vacuum pump is vented to the gas collection system. The vacuum pump is used to draw any residual liquid from a sampling valve and to remove droplets from the sample retrieval lines.

FIGURE 1 Flow Diagram for the Mo-Recovery Glovebox

FIGURE 2 (A) Mo-Recovery Glovebox and (B and C) Equipment Installed per the Flow Diagram in Figure 1 (The three 16-loop TFS valves can be seen in B.)

2.1 REMOTE CONTROL OF OPERATIONS

A software program was developed that permits operation of the Mo-recovery process remotely. The data-acquisition and remote-control software was implemented in the National Instruments LabVIEW development environment. Programming of the LabVIEW system to remotely control all of the solenoid valves and capture process values began late in the second quarter of FY13. Control of the solenoid valves was accomplished early in the third quarter of FY13. Modifications to the data-acquisition and remote-control program were made during the fourth quarter of FY13.

The system can be operated either in automated or manual mode. In manual mode, a user has full control of all of the liquid solenoid valves and the air-actuated sampling valves. During automated mode, the user simply presses the NEXT STEP button, seen on the right side of Figure 3. With each press of the button, the solenoid valves relevant to the current step in the process are opened and unused valves are closed. The 24 VDC solenoid valves are controlled using quad-format solid-state relays from Measurement Computing Corp. Figure 4 shows the area of the program that is used to control the three sampling valves.

The program captures the temperatures of the upper and lower pre-heaters and the column. The system also records the conductivity, pH, and turbidity values from the target-solution-monitoring glovebox during solution irradiation. In addition, the program also records the values of the load cells serving the dump tank and the pressure gauges in the gas collection system. All values are time-stamped. To facilitate documentation of an experimental run, several comment boxes are available for users to enter time-stamped comments.

FIGURE 3 Screen Capture of the Data Acquisition and Remote Control Program Written in the LabVIEW Environment

FIGURE 4 Screen Capture of the Program Tab That Is Used to Control the Mo-Recovery Sampling Valves

3 CONCENTRATION COLUMN SETUP

A down-scaled concentration column of the SHINE Mo-99 full scale production column was designed and built for the mini-SHINE experiment (Figure 5). In this process, the Mo-99 strip solution in 0.1 M sodium hydroxide (NaOH) will be acidified to pH 2 and passed through a S40 titania 1-cm inner diameter (I.D.) $\times$ 1-cm-long column. The details of the experimental conditions are summarized in Table 1. Mo-99 will be stripped from the concentration column with 24 mL of 1 M NH_4OH and then reduced to dryness and acidified to 1 M HNO_3 prior to entry into the LEU-Modified Cintichem purification process.

The concentration column experiment will be performed in the linac facility's recently installed shielded box. Figure 6 is a diagram of the concentration column setup. The feed solution containing Mo-99, the wash, and strip solutions will be drawn through a 5-way valve using a positive-displacement pump. The feed and strip solutions will be heated to 80°C and 70°C, respectively, using an inline solution pre-heater. Three-way Swagelok valves and 3-way Hamilton valves will be utilized to enable flow in the up-flow or down-flow direction through the column or the column bypass. The column utilized will be a 10-mm I.D. $\times$ 100-mm long Benchmark glass column equipped with quick disconnects for easy exchange for subsequent

FIGURE 4 Mini-SHINE Concentration Column Setup

TABLE 1 Process Conditions for Mini-SHINE Concentration Column Experiment

Column I.D. (cm)	MTZ _{0.1%} (cm)	Column Length (cm)	Column Volume (mL)	Sorbent Weight (g)	Velocity (cm/min)	Flow Rate (mL/min)	Loading Time (min)	Solution Volume (mL)	Strip Volume (mL)
1	0.72	1.0	0.79	0.99	20.0	15.7	60	941	24

FIGURE 5 Diagram of the Mo-99 Concentration Column Setup

experiments. Column eluent, Mo-99 strip solution, and the washes will be collected, through a 5-way valve in septa bottles and vented to the gas collection system. Most materials are made of stainless steel (SS), polyether ether ketone (PEEK), polyethylene (PE), or butyl rubber to prevent radiation degradation.

Parts for the concentration column setup include:

1. VWR bottles, high-density polyethylene (HDPE), 4 oz. $\times$ 3 beakers, SS, 125 mL $\times$ 3
2. PEEK tubing 1/8 in., .062 in. inner diameter (I.D.), natural (Supleco, 54995)
SS tubing, 1/8 in. outer diameter (O.D.) 5-way ball valve, SS, 1/8 in. OD (Swagelok, SS-43ZFS2)
3. Solution pre-heater, 110 VAC 65W/350°C (VICI HCE1)
4. 3-way 40G ball valve, SS, 1/8 in. O.D. (Swagelok, SS-41GXS2) $\times$ 2

5. Inert Valve 3 HOUS/3PLUG (Hamilton 8677) $\times$ 2
Adapter, SS 1/8–.060 in. (Supleco, 58743) $\times$ 6
6. Benchmark column, 10 mm/100 mm 1 x F 1 x A (Omnifit, 006BCC10-10AF)
Miniature quick connect, 1/8 in. tube (Swagelok, SS-QM2-B-200) $\times$ 2
7. FMI pump
Male connector, SS, 1/8 in. (Swagelok, SS-200-1-2) $\times$ 2
8. 5-way ball valve, SS, 1/8 in. O.D. (Swagelok, SS-43ZFS2)
Polytetrafluoroethylen (PTFE) ferrule set for 1/8 in. (Swagelok, T-200-SET)
PEEK tubing 1/8 in., 062 in. I.D., natural (Supleco, 54995)
9. Female connector, SS, 1/8 in. tube (Swagelok, SS-200-7-2) $\times$ 5
Luer-to-threaded National Pipe Thread (NPT) connector, male,
LU (Supleco, Z514691) $\times$ 5
Syringe needles, SS 304, ST (Sigma-Aldrich Z126756-12EA) $\times$ 5
60-mL vials with PP closures and butyl rubber septa
10. Pyrex 1-L bottle, grad, open top cap and butyl rubber septa

4 Micro-SHINE TRACER COLUMN RESULTS

A uranyl-sulfate micro-SHINE solution containing 1 ppm iron sulfate (FeSO_4) was irradiated on September 3, 2013, and used as a spike for a depleted uranyl-sulfate solution containing 3 μM stable Mo, added as sodium molybdate (Na_2MoO_4). The Mo-recovery operation began 18 hours after the end of the micro-SHINE irradiation. A 0.66-cm I.D. $\times$ 3-cm long column was packed with a pure titania sorbent made up of 110 μm particles with 60 Å pores. Approximately 260 mL of a uranyl-sulfate solution containing an irradiated micro-SHINE solution (2 mL) and 3 μM stable Mo was passed through the column in 2 hours. After the feed solution was loaded onto the column at a flow rate of 2.2 mL/min, the column was washed with 10 column volumes (CV) of 0.1 M H_2SO_4 and 10 CVs of H_2O in the up-flow direction. The column and all solutions were heated to 80°C. Mo was recovered by passing 30 CVs of 0.1 M NaOH at 1 mL/min through the column in the down-flow direction. Table 2 shows the gamma counting results for the fission products that had clean peaks and showed accurate decay patterns over a period of 3 days for the various streams. Gamma counting results were $\pm 5\%$, and the majority of Mo-99 was recovered in strips 2 and 3, which indicates that less than 30 CVs of 0.1 M NaOH is required to achieve a high Mo-recovery yield. Mo-recovery is highly dependent on pH, and once the column reaches a pH >10 , Mo elutes fairly quickly ($\sim 100\%$ in 13 CVs). These data show that less volume is needed for entry into the concentration column operation, which will take less time for entry into the LEU-Modified Cintichem purification process. Previous experiments showed that the Mo product volume would contain 20 to 30 CVs for entry into the concentration column; however, it now appears that 10 to 15 CVs are sufficient. Less feed volume will require a smaller concentration column, which will decrease processing time and allow for quicker entry into the purification process.

It is important to note that these data also indicate that Mo(VI) has not been reduced to Mo(IV) or Mo(V) under the micro-SHINE irradiation conditions, because all Mo adsorbed on the titania column and was easily recovered using 0.1 M NaOH. A significant amount of zirconium (Zr) ($\sim 65\%$) remains adsorbed on the column with about half of the iodine, which is consistent with previous tracer tests performed using the same titania sorbent. One surprising result is the fact that tellurium-132 (Te-132) did not adsorb on the titania column, which contradicts previous tracer test results showing that Te adsorbs as well as Mo on the titania sorbent. The irradiation environment may have changed Te's chemistry, thereby removing its ability to adsorb on titania.

The column effluent was then treated with a mixture of barium nitrate ($\text{Ba}(\text{NO}_3)_2$) and strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) to convert the uranyl-sulfate solution to a uranyl-nitrate solution. These results are discussed in the report entitled *FY-13 Progress Report on the Cleanup of Irradiated 130 g-U/L Uranyl Sulfate SHINE Target Solutions*, which was also an end-of-year report.[Bennet]

TABLE 2 Gamma Counting Results for the Micro-SHINE Tracer Column Experiment

Stream	Sr-91	Zr-97	Mo-99	Ru-103	Rh-105	I-131	Te-132	I-133	Ba-140	Ce-141	Ce-143
Effluent	91	33	0	100	100	29	100	3	100	100	100
Acid wash	-	2	-	-	-	-	-	-	-	-	-
Water wash 1	-	-	-	-	-	-	-	-	-	-	-
Strip 1 (1–6 CVs)	-	-	-	-	-	-	-	-	-	-	-
Strip 2 (7–14 CVs)	-	0.2	83	-	-	4	-	17	-	-	-
Strip 3 (15–20 CVs)	-	-	18	-	-	8	-	16	-	-	-
Strip 4 (21–30 CVs)	-	-	2	-	-	-	-	11	-	-	-
Water wash 2	-	-	-	-	-	-	-	-	-	-	-
Amount left on column	9	65	0	0	0	59	0	53	0	0	0

5 CONCLUSIONS AND FUTURE WORK

Cold testing of the Mo-recovery and concentration column setups is scheduled for the week of October 14, 2013.

The 5 L of sodium bisulfate (NaHSO_4) spiked with 100 mCi of Mo-99 will be irradiated the week of October 21, 2013. The solution will be passed through an initial Mo-recovery column, and samples will be collected during irradiation. These steps will be conducted remotely, but sample retrieval will be done manually. The Mo-product solution will be acidified and passed through a concentration column, and the final product from the concentration column will be purified using the LEU-Modified Cintichem process. The concentration column and purification processes will be performed in a hot cell in the linac facility using manipulators.

After the 5-L NaHSO_4 experiments are complete, 5 L of uranyl sulfate (LEU; 19.8% U-235; 140 g-U/L) will be irradiated several times for short periods of time to gain an understanding of gas generation rates, pH changes in solution, and solution volume loss. After several short irradiations have been performed, the 5 L solution containing 3 μM stable Mo, added as Na_2MoO_4 , will be irradiated for 14 hours, which will produce ~ 2 Ci Mo-99. The solution will be passed through an initial Mo-recovery column (2-cm I.D. $\times$ 10-cm long) at a flow rate of 40 mL/min. The solution and column will be heated to 80°C. The column will be washed with 10 CVs of 0.1 M H_2SO_4 and 10 CVs of H_2O . Mo will be recovered using 10 to 15 CVs of 0.1 M NaOH. Samples will be collected remotely during the column process and retrieved manually at least 24 hours post-irradiation. The Mo-product solution will be acidified using nitric acid and passed through a titania concentration column. Mo will be recovered using 1 M NH_4OH heated to 70°C. The Mo-product solution will be purified using the LEU-Modified Cintichem process. The final purified product will be shipped to a technetium-99m (Tc-99m) generator manufacturer. The concentration column and purification processes will be performed in a hot cell in the linac facility using manipulators. The 5 L uranyl-sulfate 14 hour irradiation and subsequent Mo-recovery columns and purification process will be performed at least 4 times.

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