AMORE Mo-99 Spike Test Results

Nuclear Engineering Division

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by

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1. INTRODUCTION

With funding from the National Nuclear Security Administrations Material Management and Minimization Office, Argonne National Laboratory (Argonne) is providing technical assistance to help accelerate the U.S. production of Mo-99 using a non-highly enriched uranium (non-HEU) source. A potential Mo-99 production pathway is by accelerator-initiated fissioning in a subcritical uranyl sulfate solution containing low enriched uranium (LEU). As part of the Argonne development effort, we are undertaking the AMORE (Argonne Molybdenum Research Experiment) project, which is essentially a pilot facility for all phases of Mo-99 production, recovery, and purification. Production of Mo-99 and other fission products in the subcritical target solution is initiated by putting an electron beam on a depleted uranium (DU) target; the fast neutrons produced in the DU target are thermalized and lead to fissioning of U-235. At the end of irradiation, Mo is recovered from the target solution and separated from uranium and most of the fission products by using a titania column. The Mo is stripped from the column with an alkaline solution. After acidification of the Mo product solution from the recovery column, the Mo is concentrated (and further purified) in a second titania column. The strip solution from the concentration column is then purified with the LEU Modified Cintichem process. A full description of the process can be found elsewhere [1–3].

The initial commissioning steps for the AMORE project include performing a Mo-99 spike test with pH 1 sulfuric acid in the target vessel without a beam on the target to demonstrate the initial Mo separation-and-recovery process, followed by the concentration column process. All glovebox operations were tested with cold solutions prior to performing the Mo-99 spike tests. Two Mo-99 spike tests with pH 1 sulfuric acid have been performed to date.

Figure 1 shows the flow diagram for the remotely operated Mo-recovery system for the AMORE project. There are two separate pumps and flow paths for the acid and base operations. The system contains three sample ladders with eight sample loops per ladder for target mixing; column loading, including acid and water washes; and column stripping, including the final water wash.

FIGURE 1. Flow diagram for the AMORE separation system housed in a shielded glovebox.

2. RESULTS AND DISCUSSION

2.1 Sample Retrieval Problems and Solution

Results have shown a 10–20% dilution effect for samples retrieved by means of the sample loops; in other words, 10–20% of residual solution is left in the loops after they have been “emptied.” Additionally, after the loops were washed three times and samples were retrieved after each wash, the loops still contained residual solution. With this in mind, a nitrogen purge of all loops prior to washing was added for the second Mo-99 spike test and helped to remove more residual Mo-99 activity compared to the amount of residual activity found in the first Mo-99 spike test, when samples were not purged with nitrogen.

In the first Mo-99 spike test, the target mixing samples showed that 13% of the original Mo-99 activity remained in the loops after they were flushed with acid for 1 minute. After a second wash of the loops with acid for 1 minute, a third set of samples showed that 0.08% of the original activity remained.

For the column loading loops, the Mo-99 activities found in the samples after the first and second washes were below minimum detectivities ($<9 \times 10^{-4}$ μCi). For the column stripping samples, washing the loops twice with water for 1 minute and retrieving samples after each wash showed that 7% and 4% of the Mo-99 found in the original sample remained.

In an effort to remove more residual Mo-99 during the washing steps, after each set of samples was retrieved, all of the loops were purged with N_2 prior to being washed with liquid for the second Mo-99 spike test. For the target mixing samples, 2% of the original Mo-99 activity remained after the loops were purged with N_2 and washed with acid for 1 minute. The target mixing loops were purged with N_2 and washed with acid for 1 minute a second time, and 0.8% of the original activity remained. The column loading samples that were retrieved after purging with N_2 and washing with acid for 1 minute were reported as minimum detectivities ($<4 \times 10^{-4}$ μCi). After a single purge with N_2 and a water wash for 1 minute, 0.9% of the original Mo-99 activity remained in the column stripping loops. After a second purge with N_2 and a water wash for 1 minute, 0.03% of the original Mo-99 activity remained in the loops.

Results from the two spike tests are discussed below.

2.2 First Spike Run

Table 1 shows the results for the first Mo-99 spike test. The Mo-99 activity in the target mixing samples retrieved via the target mixing ladder was at least 15% low based on the amount of activity found in the recovery column (RC) product or feed for the concentration column (CC). The RC feed sample taken from the verification tank gave an artificially high Mo-99 activity because the same 1/16th-in. tubing that was used to introduce the Mo-99 spike into the verification tank was used to retrieve the feed sample. Little to no activity was found in the column effluent, acid wash, or water wash samples for the RC and CC operations.

Due to an issue with LabView shutting down, a final water wash of the column was not done for the first Mo-99 spike test. The percent Mo-99 recovered values are based on the single collected feed sample of 47 mCi, which explains why the Mo-99 recoveries for the CC feed and CC product are >100%. Some of the individual samples were not retrieved because the vacuum pump trap was holding too much vacuum, which prevented some of the solenoid valves from opening. A smaller trap was installed for the second Mo-99 spike test.

TABLE 1. Gamma counting results for samples retrieved from the first Mo-99 spike test.

Sample	Mo-99 Activity (mCi)	% Mo-99*
Target Mixing Feed – RC	47	100
Column Effluent – RC	0.03	0.06
Acid Wash – RC	0.004	0.01
Water Wash – RC	0.02	0.05
Mo-99 Product – RC/ Feed – CC	55	117
Column Effluent – CC	0.01	0.02
Acid Wash – CC	0.0004	0.001
Water Wash – CC	0.0005	0.001
Mo-99 Product – CC	55	118
Waste – CC	0.04	0.07

* %Mo-99 is based on the target mixing feed sample, which does not accurately represent the Mo-99 activity loaded onto the RC.

Figure 2 shows stripping data for the Mo-99 product eluted from the titania RC for the first Mo-99 spike test based on stripping samples that were retrieved via the column stripping ladder in the AMORE glovebox. Results indicate that the majority of the Mo-99 is recovered in the first ~700 mL of 1 M NaOH, which is surprising because the base heater was not working for this experiment. The column was heated to 80°C, but the strip solution was not heated. The amount of strip solution represents 5.6 column volumes (CVs) and suggests that significantly less strip solution (when 1 M NaOH is used) is required to strip the Mo-99 product from the RC. If the final Mo-99 spike test shows the same type of behavior, the amount of strip solution may be decreased to 10 CVs from 20 CVs for the AMORE experiments with uranyl sulfate.

FIGURE 2. A plot of NaOH volume versus Mo-99 activity based on the column stripping samples collected via the column stripping ladder in the AMORE glovebox.

2.3 Second Spike Run

Table 2 shows the results for the second Mo-99 spike test. A sample was taken from the verification tank after the Mo-99 spike was added, and the solution was thoroughly mixed for 2 hours. The verification tank sample collected for the second Mo-99 spike test was taken via an external vessel and did not employ the same tubing that was used to introduce the Mo-99 spike into the verification tank. Once the uranium irradiations began, a feed sample could not be taken until after irradiation when entry into hot cell one is allowed. For this Mo-99 spike test, a few hundred milliliters of feed solution was purposely not loaded on the column to test a different way of retrieving a feed sample for future irradiations with uranium. The solution remaining in the target vessel was pumped into the verification tank, and the solution was circulated in a loop that goes in and out of the verification tank. A sample was taken via the syringe port manually; however, the Mo-99 activity in this sample was ~50% low. Based on these results, it appears that either the loop was filled with acid solution, or the path from the target vessel to the verification tank was filled with acid prior to the solution being pumped from the target vessel, causing the activity to be ~50% low. For the next Mo-99 spike test with beam on target, all paths will be purged with N₂ prior to pulling the unloaded solution from the target vessel to the verification tank.

The Mo-99 product from the RC or the feed for the CC showed low activity because the air purge line to mix the solution in the BigFoot hot cell had cracked, and the solution was not mixed prior to collecting a sample. Little to no activity was found in the column effluent, acid wash, or water wash samples for the RC and CC operations. Results from the overall process show that 92% Mo-99 was recovered. During this test, there were still issues with the sample retrieval process related to the column stripping ladder. Only four of the eight samples were

retrieved each time during actual sample retrieval and sample retrieval during the washout steps. Part of the 1/16th-in. tubing appeared to be kinked, and the sampling manifolds needed to be re-done for several of the loops on the column stripping ladder. These issues will be remedied before the next Mo-99 spike test with beam on target.

TABLE 2. Gamma counting results for samples retrieved from the second Mo-99 spike test.

Sample	Mo-99 Activity (mCi)	% Mo-99*
Verification Tank Feed – RC	37	100
Target Mixing Feed – RC	30	81
Unloaded Feed in Target Vessel via Syringe Port – RC	19	51
Column Effluent – RC	0.06	0.2
Acid Wash – RC	0.003	0.01
Water Wash – RC	0.03	0.08
Mo-99 Product – RC/Feed – CC	26	70
Acid Wash – CC	0.0005	0.001
Water Wash – CC	0.0300	0.08
Mo-99 Product – CC	34	92
Waste – CC	0.03	0.08

* %Mo-99 is based on the verification tank feed sample, which is accurately represents the Mo-99 activity loaded onto the RC.

Figure 3 shows the stripping data for the Mo-99 product eluted from the titania RC for the second Mo-99 spike test based on stripping samples that were retrieved via the column stripping ladder in the AMORE glovebox. The strip solution prior to entry on the column and the column itself were both heated to 80°C. Results indicate that the majority of the Mo-99 was recovered in the first ~1100 mL of 1 M NaOH. This represents 8.8 CVs and suggests that less strip solution (when 1 M NaOH is used) is required to strip the Mo-99 product from the RC. For the final Mo-99 spike test with beam on target, the amount of strip solution will be decreased to 10 CVs from 20 CVs.

FIGURE 3. A plot of NaOH volume versus Mo-99 activity based on the column stripping samples collected via the column stripping ladder in the AMORE glovebox.

3. CONCLUSIONS

Overall, the amount of Mo-99 recovered from the RC and CC operations for the first two spike tests was good. In the first Mo-99 spike test, it is difficult to determine the overall %Mo-99 recovery because we do not have a good value for the feed solution; however, if we assume the target mixing sample is 20% low, the amount of Mo-99 loaded onto the RC would be 56.4 mCi. With 55 mCi Mo-99 recovered in the CC product, the overall recovery would be 98%. The amount of Mo-99 recovered in the second Mo-99 spike test was 92%. Comparing Figures 2 and 3, the $\mu\text{Ci/g}$ Mo-99 in the first strip sample for spike test #1 and spike test #2 are significantly different. In the first spike test, the activity was 178 $\mu\text{Ci/g}$ in the first strip sample, and in the second spike test, the activity was 6 $\mu\text{Ci/g}$. Also, in the first spike test, less strip solution was required to fully strip Mo-99 from the RC compared to the second spike test. The fact that the strip solution was not heated in the first spike test makes these results even more surprising. With the strip solution being heated to 80°C in the second spike test, the first strip sample may not have been taken early enough in the strip process to see the higher activity. In the next Mo-99 spike test, samples will be taken earlier than 5 minutes after stripping at 84 mL/min. Nonetheless, strip results from both spike tests suggest less than 20 CVs of 1 M NaOH can be used to fully remove Mo-99 from the RC.

Lessons were learned during the first two spike tests related to removal and installation of the verification tank, column, and effluent cart. Additionally, the sample retrieval process is still being improved, and new needle assemblies will be built for the column stripping ladder for the next Mo-99 spike test with beam on target. A third spike test will be performed to test these improvements before uranium irradiation experiments begin.

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