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SHINE Chemistry Overview

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ABSTRACT

As part of the Material Management and Minimization (M^3) Mo-99 Technology Development program, Argonne is helping to accelerate the domestic production of Mo-99. The work being done at Argonne supports SHINE Medical Technologies in their efforts to produce fission-product Mo-99 via an accelerator-driven process. Argonne's mini-SHINE experiments will produce 2 Ci (phase 1) and 20 Ci (phase 2) of Mo-99 for shipment to SHINE's potential Tc-99m generator manufacturer partners. Mo-99 will be produced using a low-enriched uranium (LEU) uranyl-sulfate target solution, an electron linac, and a tantalum (phase 1) or depleted-uranium target (phase 2) for neutron production. Results from the phase 1 mini-SHINE experiments show a delay in oxygen generation, indicate no change in Mo oxidation state, and prove that the final Mo-99 product does meet required purity specifications. Once the Mo-99 product is shipped to GE Healthcare, phase-1 equipment will be removed and phase 2 will be installed at Argonne.

1. Introduction

Argonne National Laboratory is involved in the development of many of the chemistry-related activities associated with the SHINE system. Earlier efforts included the development of a procedure for preparing uranyl-sulfate solution from LEU (low-enriched uranium) metal, column for the separation and recovery of Mo-99 from a uranyl sulfate solution, and method for conversion of uranyl sulfate to uranyl nitrate required for clean-up activities [1-5]. More recent work has been devoted to the mini-SHINE experiments, which represent a mini-pilot plant for the SHINE process. The mini-SHINE system includes a gas collection and analysis system, target solution glovebox, Mo-recovery glovebox, shielded cell that houses the target solution, and a separate hot cell used for the concentration column, evaporation, and LEU-Modified Cintichem purification processes. Samples are collected during irradiation, the Mo-recovery

operation, and all secondary purification steps performed in a separate hot cell. Samples collected during all processing steps are retrieved and gamma counted to determine Mo-recovery yields, production rates, and impurity levels.

Results from the phase-1 mini-SHINE experiments show that there is a delay in oxygen production during the first 2 - 3 hours of irradiation. Air is purged into the mini-SHINE system to keep the hydrogen concentration below 1% during this time. Mo-recovery results show that Mo does not change oxidation state when exposed to a maximum power density of ~0.05 kW/L for phase 1 experiments. Precipitation of fission products and/or formation of uranyl-peroxide solids have not been observed at the phase-1 power densities. Four irradiations with complete processing have been performed, and Mo-99 purity specifications were met for three out of the four final products.

Mo production rates for the first five irradiations were much lower than expected based on MCNPX calculations. A camera was put in place to examine the beam alignment on the target. Because the beam was properly hitting the target, the next step was to examine the target solution. It was determined that the concentration of the target solution had decreased from ~140 g-U/L to 93.7 g-U/L due to an inadvertent dilution and solution loss. The solution will be reconstituted to bring the concentration back to 140 g-U/L. A 2 - 4 hour irradiation will be performed to determine the production rates for a LEU uranyl-sulfate solution at 140 g-U/L. Once production rates have been determined, a long irradiation will be done with full processing and shipment of the final purified Mo-99 product to GE Healthcare in the UK. A second short irradiation will also be performed to examine peroxide formation as part of the micro-SHINE setup at the linac. Uranyl-peroxide precipitation experiments could not be repeated using the Van de Graaff accelerator, where a significant amount of uranyl peroxide precipitated during experiments in 2012 [6-7]. Once these three irradiations are completed, phase-1 equipment, gloveboxes, target, and target vessel will be removed. Phase 2 installation includes a single glovebox, new depleted-uranium target, new target vessel, and an additional 15-L of 140 g-U/L uranyl-sulfate solution. Phase-2 experiments will include several irradiations including a production run with shipment to Lantheus Medical Imaging. Data collected for the phase-2 experiments will be closer to the power densities expect for the real SHINE system at ~0.5 kW/L.

2. Experimental

2.1 Mini-SHINE Irradiations

To date, three Mo-99 spike runs and five irradiations have been performed using an LEU uranyl-sulfate solution and Argonne's linac. Approximately 5-L were irradiated in a 304SS target solution vessel located in a shielded cell. A large amount of bubbles formed in the uranyl-sulfate solution during irradiation, making the pH, conductivity, and turbidity measurements unreliable. These tools will not be a part of the phase 2 mini-SHINE experiments. Gases generated during radiolysis were analyzed using a GC-MS (gas chromatography-mass spectrometer), RGA (residual gas analyzer), and H_2 sensor. Uranyl-sulfate solutions containing stable Mo added as sodium molybdate with tracer Mo-99 (no irradiation) and without tracer Mo-99 (irradiation) were passed through a titania column, and the Mo product was transferred directly to a second hot cell for further processing. All glovebox operations were performed remotely using LabView

software. Samples were retrieved manually at least 8 hours after irradiation. The Mo product was acidified and passed through a second concentration column. The Mo-product from the concentration column was acidified before entering the LEU-Modified Cintichem purification process. Full processing was done for three Mo-99 spike runs and four irradiations.

2.2 Preparation of Mo-99 Spike Solution

Mo-99 used for the Mo-99 spike runs is removed from a Tc-99m generator by placing a serum vial containing 1 M NH_4OH on the needle labeled "Saline Charge". Then an evacuated serum vial is placed on the needle labeled "Receiver". The Mo-99 spiked solution is prepared by bringing the solution to dryness on a hot plate, and re-dissolving it in 0.1 M H_2SO_4 containing stable Mo as Na_2MoO_4.

2.3 Gamma Counting of Mo-99 and Other Fission Products

Fission product activities in the samples retrieved 8-24 hours post-irradiation were determined using a high purity germanium detector. Mo-99 was quantified by measurement of its 181 keV and/or 739 γ-rays. The activities of Mo-99 and all other fission products were corrected for decay.

2.4 Gas Analysis System

The objectives of the mini-SHINE experiments are to quantify production rates and determine the composition of radiolytic gases generated during operation of the system under varying conditions of power density, solution temperature, and startup conditions. Gases of particular interest are hydrogen and oxygen.

The experiment consists of three interconnected systems, a target solution vessel, a gas analysis system, and a gas collection system, as shown in Figure 1. The target solution vessel houses the LEU uranyl sulfate solution. Neutrons are emitted from a tantalum target located in a dry well in the center of the solution. Headspace gases are recirculated through a catalyst bed that recombines the hydrogen and oxygen. The gas analysis system has a gas chromatograph (GC) with a mass spectrometer detector (MS) and thermal conductivity detector (TCD) for periodic sampling and a residual gas analyzer (RGA) for continuous monitoring of the target solution vessel headspace. The gas collection system collects and stores gases for decay storage and safe disposal; it also keeps the entire system at sub-atmospheric pressure (Figure 2) and (Figure 3) show the instrumentation and gas analysis apparatus, respectively.

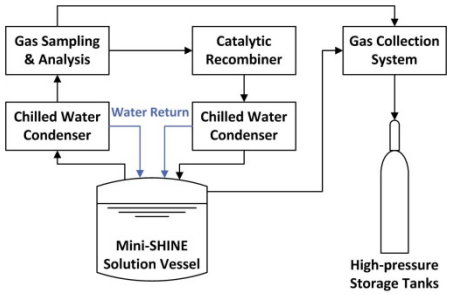

Figure 1. Block diagram of the mini-SHINE gas analysis and collection system.

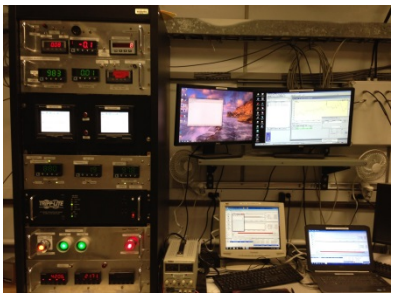

Figure 2. Mini-SHINE gas analysis & collection instrumentation.

Figure 3. Micro- and mini-SHINE gas analysis enclosure.

3. Results

3.1 Mo-99 Spike Runs

To date, three Mo-99 spike runs (no irradiation) have been performed using an LEU uranyl sulfate solution. After 50% of the Mo did not load on the column during the first Mo-99 spike run, it was determined that there was a problem with the mini-SHINE system not with the column performance. The solenoid valves in the mini-SHINE system can only withstand a backpressure of about 12 psi, but they can withstand a pressure of ~70 psi in the forward direction. They remain open and continue to leak when exposed to 12 psi or higher of backpressure, which occurs during column loading as the target solution is loaded in the up-flow direction. The valves potentially exposed to 12 psi or higher of backpressure have since been doubled up to allow up to 70 psi in both directions and prevent leaking. This is what caused about 50% of the Mo to not load on the column during the first Mo-99 spike run. During the second Mo-99 spike, 88% of the Mo-99 was recovered after the initial recovery column. Results from the third Mo-99 spike run showed that 98% of the Mo-99 was recovered after the first titania column.

Results from the Mo-99 spike runs with non-irradiated uranyl sulfate solution showed that there were problems with the mini-SHINE system. Lessons learned during the Mo-99 spike runs included: 1. Solenoid valves can only withstand 12 psi of backpressure and valves that were exposed to solutions passing through in both directions were doubled up., 2. The sunflower valves originally used to collect samples leak and were replaced with solenoid valves, and 3. Sufficient mixing of the feed solution prior to loading it on the column is required to obtain reliable data related to Mo-99 recoveries.

3.2 Irradiations

Five irradiations have been performed using an LEU uranyl-sulfate solution and Argonne's linac. Irradiation times varied from 2 – 32 hours, and Mo production quantities ranged from >70 – 810 mCi Mo-99 at end of bombardment (EOB). Table 1 shows the results where overall Mo-99 recoveries ranged from 42-95%. Because greater than 80 mCi Mo-99 was found in the final product after the initial recovery column, the amount of Mo-99 produced at EOB for the first irradiation was definitely greater than 70 mCi. The overall yield of 95% was based on the Mo-99 activity in the product from the first titania column. Mo-99 activity in the feed solution for the first spike run was low due to insufficient mixing in the target vessel loop. A step was added to all subsequent irradiations to ensure sufficient mixing. The mixing issue was resolved for the second irradiation; however, the overall yield decreased to 86%. The overall yield for the third irradiation was good at 94%, but purity specifications for the final product were not met for Ru. Mo-99 purity specifications were still met for all other potential contaminants for the final product from the third irradiation. Table 2 shows the Mo-99 purity specifications required by both the European and British Pharmacopoeias. Total gamma results are not included in the purity specification results, and due to the short half-lives of the Sr isotopes, Ba-140 was used to track Sr. The ratio of Ru-103 to Mo-99 in the final product was 1.74×10^{-4}, which is most likely due to one or more of the following reasons. First, the Mo-product from the initial recovery column was eluted with 1 M NaOH instead of 0.1 M NaOH in an effort to reduce the volume of Mo-strip solution. This may have changed the chemical form of Ru, which allowed more Ru to co-elute with Mo in the product. Build-up of Ru-103 (39.4 d half-life) in the uranyl-sulfate solution from previous irradiations may have played a role as well. For the fourth irradiation, Mo was eluted from the initial recovery column using 0.1 M NaOH. Additionally, in the Cintichem process, the solution was contacted with potassium permanganate for a longer period of time to ensure Ru was in the proper chemical form for removal from the final product. Ultimately, this extended contact time with permanganate destroyed a significant portion of the Mo-ABO product, which resulted in a recovery of only 42%. All purity specifications were met for the final product from the fourth irradiation, but the recovery was low. The total alpha results show $<10^{-10}$ Ci-α/Ci-^{99}Mo for all of the four Mo-99 products.

Table 1. Results for the mini-SHINE LEU irradiations.

Irradiation	Time (hr)	Mo-99 produced (mCi)	Met Purity Specs[2]	Overall Mo-99 Yield
1	2	70[1]	Yes	95%
2	8	350	Yes	86%
3	32	810	No[3]	94%
4	20	380	Yes	42%[4]
5	12	190	-	-

1. Insufficient mixing
2. Purity specifications do not include total gamma results
3. Purity specifications not met for Ru
4. Modifications made to Cintichem to remove Ru from previous irradiation – longer contact with $KMnO_4$ – destroyed ABO-Mo complex

Table 2. Mo-99 purity specifications set by the European and British Pharmacopoeias.

Ratio (X/Mo^{99})	Product Specification

$^{131}I/^{99}Mo$	$\leq 5\times10^{-5}$
$^{103}Ru/^{99}Mo$	$\leq 5\times10^{-5}$
$^{132}Te/^{99}Mo$	$\leq 5\times10^{-5}$
^{89}Sr & $^{90}Sr/^{99}Mo$	$\leq 6\times10^{-7}$
$\Sigma\alpha/^{99}Mo$	$\leq 1\times10^{-9}$
$\Sigma\gamma/^{99}Mo$	$\leq 1\times10^{-4}$

3.3 Modifications to LEU Modified Cintichem Process

In an effort to increase Mo-99 yield by reducing time, two major modifications were made to operations in the second hot cell. Originally, the Mo-product from the concentration column was brought to dryness via simple evaporation and acidified prior to entry into the LEU-Modified Cintichem process. The Mo-product from the concentration column is no longer evaporated but acidified directly using 10 M nitric acid. This approach saves about 3 – 4 hours of time, which equates to 3 – 4% more Mo in the final product. A single silver-charcoal column was removed from the LEU Modified Cintichem process to save time without affecting the purity specifications for the final product.

3.4 Gas Analysis Results

The mini-SHINE system is kept slightly negative by a 2-pump/3-tank off gas collection system. Gases generated during irradiation are measured continuously using an RGA, and results are shown below (Figure 4) for hydrogen and oxygen generation during the second LEU uranyl sulfate irradiation. Oxygen is not observed during the first few hours, and air was bled into the system to keep the hydrogen concentration below 1%. It is also important to state that the major fraction of radioiodine stays in the solution during operation because very little iodine was found in samples collected from the gas collection system.

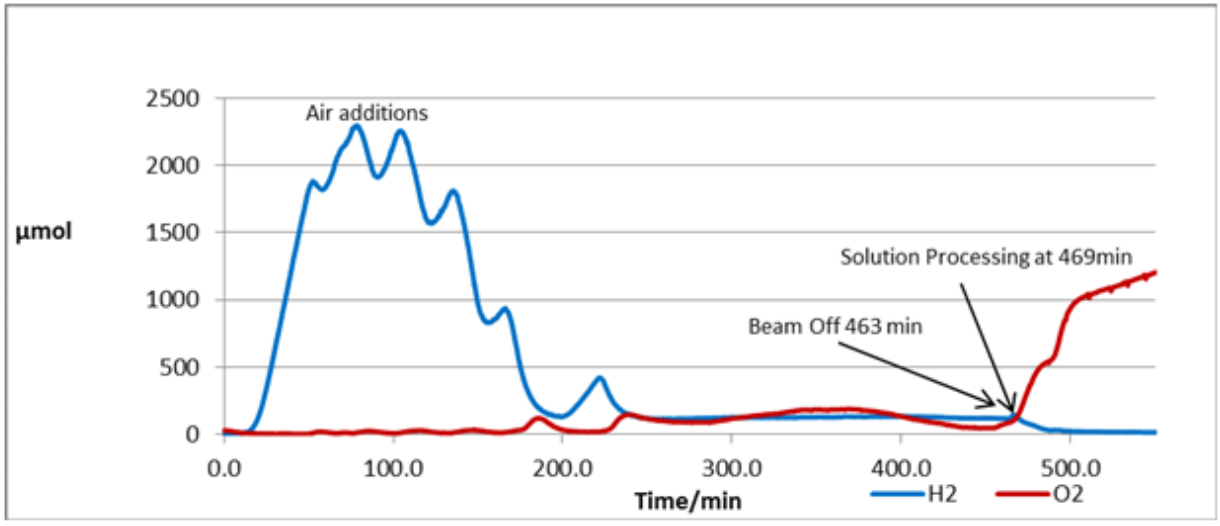

Figure 4. Hydrogen and oxygen generation rates during the second LEU uranyl sulfate irradiation.

3.5 Fission Product Partitioning on Titania

Results from the four irradiation experiments show slightly different results than what was predicted based on batch studies and tracer tests [9]. Table 4 shows fission product partitioning results for the first titania column after the LEU solution from the second irradiation was passed through the column. It was expected than greater than 90% Te remained adsorbed on the titania column, but the results show, only about 30% remains adsorbed on the titania. As expected most of the Zr remains adsorbed on the titania column. Other isotopes that remain adsorbed on the first titania column include Ru (~40%), Ce (~15%), Sb (~5%), and some iodine mainly from the decay of adsorbed Te isotopes. Isotopes found to co-elute with the Mo-product include Ru, I, and Sb. Values of zero are shown for isotopes that had exceeded 12 half-lives when samples were gamma counted or had high counting errors associated with them. Column effluent #3 was collected after one hour of column loading.

Table 3. Fission product partitioning on the first titania column for the second LEU uranyl sulfate irradiation.

Isotope	Average Feed (mCi)	Column Effluent #3(%)	Acid Wash (%)	Water Wash #1 (%)	Mo-Product (%)
Zr-95	1.63E+01	6.40E-01	1.98E-03	0.00E+00	0.00E+00
Nb-95	daughter	daughter	daughter	daughter	daughter
Mo-99	3.48E+02	0.00E+00	0.00E+00	0.00E+00	9.36E+01
Ru-103	1.46E+01	4.87E+01	2.28E+00	4.58E-01	7.34E+00
I-131	2.34E+01	2.68E+01	1.34E+00	1.52E+00	1.52E+02
I-133	4.25E+02	9.00E+00	0.00E+00	0.00E+00	1.71E+02
Cs-136	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Cs-137	1.28E-01	0.00E+00	1.71E+00	0.00E+00	0.00E+00
Ba-140	8.19E+01	6.79E+01	1.39E+00	2.37E-02	0.00E+00
Ce-143	6.79E+02	8.23E+01	0.00E+00	0.00E+00	0.00E+00
Zr-97	1.14E+03	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Te-132	2.66E+02	6.66E+01	3.55E+00	0.00E+00	0.00E+00
Nb-97	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Rh-105	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sn-125	2.13E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sb-127	1.47E+01	8.67E+00	1.20E+00	4.53E-01	6.86E+00
Sr-91	2.16E+03	9.96E+01	0.00E+00	0.00E+00	0.00E+00
I-135	9.99E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Np-239	6.50E+02	8.25E+01	1.66E+00	0.00E+00	0.00E+00
U-237	5.65E+01	8.19E+01	1.46E+00	0.00E+00	0.00E+00
Te-131m	6.07E+01	1.02E+02	0.00E+00	0.00E+00	0.00E+00
I-132	2.27E+02	6.23E+01	5.15E+00	0.00E+00	0.00E+00
Eu-156	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
La-140	6.20E+01	9.01E+01	2.29E+00	3.58E-02	0.00E+00

Nd-147	3.85E+01	8.74E+01	1.53E+00	8.45E-04	0.00E+00
Pm-151	4.60E+01	8.60E+01	0.00E+00	0.00E+00	0.00E+00
Y-93	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

4. Discussion

The mini-SHINE results obtained to date show that Mo-99 purity specifications can be met, but the complex chemistries of Ru and I are the most difficult to remove from the final Mo-99 product. A task has been added to our work package to develop a better understanding of Ru and I chemistries in the SHINE processing system. For the third irradiation, by changing the concentration of the strip solution for the first recovery column, we may have changed the chemical form of Ru, making it difficult to remove from the final product. In the fourth irradiation, the concentration of the strip solution for the first recovery column was brought back to 0.1 M, and the final product did meet the purity specifications. However, the overall Mo-99 yield was low at 42%. The next mini-SHINE irradiation will be tested to ensure Mo-99 purity specifications can be met in addition to a high overall yield.

The production rates are expected to increase by at least 30% once the LEU solution has been reconstituted to 140 g-U/L. A 2 – 4 irradiation will be performed first to determine production rates and ensure the final Mo-99 product meets purity specifications with high yield. After successful completion of a shorter irradiation with the LEU solution at the proper concentration, a full-scale production run will be done with shipment of the final Mo-99 product to GE Healthcare in the UK. One more phase-1 short irradiation will be performed after this production run to look for uranyl peroxide precipitation in the micro-SHINE capsule.

After these final three phase-1 irradiations, the gloveboxes, target solution monitoring equipment, target vessel, and Ta target will be removed for installation of phase 2 mini-SHINE. Phase-2 mini-SHINE includes a single glovebox, a new depleted uranium target, a new target vessel, and an additional 15-L of target solution.

4. Conclusions

There have been several issues along the way to starting and completing the phase 1 mini-SHINE experiments. From leaky solenoid valves and sunflower sample collection valves to dilution of the uranyl sulfate target solution, a lot of lessons have been learned that should make the transition to phase 2 easier. Sending a pure Mo-99 product to GE Healthcare is an important goal for the phase-1 mini-SHINE experiments and is expected to occur very soon. A more complete understanding of the chemistry of the irradiated uranyl-sulfate solution is expected during the phase-2 experiments where power densities will be 10 times higher, and the chance for precipitation and changes in redox chemistry are more likely to occur.

5. Acknowledgements

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