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Development of the mini-SHINE/MIPS experiments

S. Chemerisov, A. J. Youker, A. Hebden, N. Smith, P. Tkac, C. D. Jonah, J. Bailey, V. Makarashvili, B. Micklich, M. Kalensky, G.F. Vandegrift
Chemical Sciences and Engineering Division
Argonne National Laboratory, 9700 South Cass Ave., 60439 Argonne, IL – USA

ABSTRACT

Argonne is assisting two of the potential domestic producers: Babcock and Wilcox Technical Services Group (B&W) and Morgridge Institute for Research (MIR) in the development of a Mo-99 production technique that uses Low Enriched Uranium (LEU). B&W is developing the Medical Isotope Production System (MIPS); in this system, the Mo-99 is produced in an LEU-fueled aqueous homogenous reactor (AHR) by the fission of U-235.

MIR is currently developing the Subcritical Hybrid Intense Neutron Emitter (SHINE), which creates Mo-99 by neutron-induced fission of LEU in a sub-critical aqueous solution. Essentially SHINE is an accelerator-driven sub-critical MIPS. One difference between the two is that MIR is currently considering aqueous uranyl sulfate solution as the target solution, while B&W is planning to use uranyl nitrate as the reactor solution.

The mini-SHINE/MIPS experiments planned at Argonne Low Energy Accelerator Facility (LEAF) will provide important design data for both systems. We will measure the production rate and composition of radiolytic gases generated during operation of the system under varying conditions of power density, solution temperature, and start-up conditions; monitor changes of solution composition (peroxide concentration, iodine and nitrogen speciation, pH, conductivity, solids formation), vs. time, temperature, and fission power; and demonstrate Mo-recovery from the irradiated solution at the end of irradiation.

In this presentation we will discuss design of the main components of the mini-SHINE/MIPS setup, results of the Monte Carlo computer simulations, and schedule and progress of the project.

1. Introduction

Under the GTRI program, Argonne is assisting three potential domestic entities to develop and implement non-HEU-based Mo-99 production in the U.S. by 2014. Two of the potential domestic producers are Babcock and Wilcox Technical Services Group (B&W) and Phoenix Nuclear Labs (PNL). The mini-SHINE/MIPS experiments described in this work will provide important design data for both systems.

MIPS Mo-99 production system development

B&W is developing the Medical Isotope Production System (MIPS) [1]. In this system, the Mo-99 is produced in an LEU-fueled Aqueous Homogenous Reactor (AHR) by the fissioning of U-235. MIPS consists of an AHR containing uranyl-nitrate solution (LEU), a molybdenum-extraction system utilizing a chromatographic column, the reactor off-gas and solution control systems. The use of AHRs presents an attractive alternative to the conventional target-irradiation method for producing Mo-99 because MIPS fuel solution itself is used to extract Mo-99 eliminating the need for targets and can operate at much lower power than required for a traditional reactor irradiating targets to produce the same amount of Mo-99. The three areas of the Argonne R&D are (1) radiolytic gas generation in the fuel solution, (2) effects of fission and radiation on reactor-solution chemistry, and (3) development and optimization recovery of molybdenum from the irradiated fuel solution.

The first solution reactors earned the name "water-boilers" because of the observed bubbling or foaming that result from the radiolytic decomposition of water by fission fragments and subsequent evolution of radiolytic gases (hydrogen and oxygen). Because nitrate ion also undergoes radiolytic decomposition, uranyl-nitrate-based AHRs will also generate nitrogen compounds from NO_2 to ammonia (N^{4+} to $^{3-}$), and N_2, NO_x, and NH_3 may be observed in the off gas. The radiolytic decomposition of nitrate ion will also have the effect of increasing the pH of the fuel solution. The rate and composition of the radiolytic gas generation is of practical importance for the design and operation of AHR for two reasons. First, the design of the reactor off-gas system depends on the generation rate and the composition of the gas stream. Second, an increase of the fuel-solution pH can lead to the formation of the precipitates and, therefore, must be controlled.

While the radiation chemistry of nitrate solutions has been investigated over the past fifty years, not much attention was given to the analysis of gas evolution especially at high radiation doses. Observations of the formation of nitrogen-containing gases under radiation are numerous, but N_2 NO_x and NH_3 formation have not been studied systematically; no mechanism for the formation of those gases was proposed. Also, the reported values of the radiolytic yields for these gases vary by an order of magnitude. The aim of off-gas measurement system of the mini-SHINE/MIPS experiments is to obtain reliable data for radiolytic gas generation in uranyl-nitrate solutions that are of practical interest to the MIPS.

SHINE Mo-99 production system development

MIR in collaboration with Phoenix Nuclear Labs (PNL) is currently developing the Subcritical Hybrid Intense Neutron Emitter (SHINE), which creates ^{99}Mo by neutron-induced fission of LEU in a sub-critical aqueous solution reactor. SHINE can produce a primary neutron flux on the order of 10^{12} n/s/cm^2 by the collision of beam of deuterium (D) ions with tritium (T) gas target and a secondary flux exceeding 10^{13} n/s/cm^2 with subcritical multiplication in the aqueous solution. Fission produced Mo-99 can be extracted from the aqueous solution and purified. Argonne tasks for SHINE development include developing an understanding of the solution chemistry under relevant operating conditions and developing the Mo-recovery and purification system. We are also assisting MIR in facility design and developing means for periodic cleanup of the recycled target solution.

2. Description of the Mini-SHINE MIPS Experiments

The mini-SHINE/MIPS experiments will be performed using the high current electron linac at Argonne LEAF facility. The experiments will use an electron/x-ray/neutron convertor to produce neutrons that will produce fission in solution. The solution will be either a 150 g-U/L LEU uranyl nitrate or 90-150 g-U/L uranyl-nitrate or uranyl-sulfate solution. In phase-1, the convertor will be tantalum, and the target solution will have a volume of five L; this will generate a fission power density of up to 0.05 W/mL. In Phase-2, the convertor will be depleted uranium, beam power will increase to 30 kW and the solution volume will be 10 to 20 L; this will generate a fission power density of up to 0.5 W/mL.

These experiments have four major objectives:

- Quantitate the production rate and composition of radiolytic gases generated during operation of the system under varying conditions of power density, solution temperature, and start-up conditions.
- Provide information on changes of solution composition (peroxide concentration, iodine and nitrogen speciation, pH, conductivity, solids formation), vs. time, temperature, and fission power.
- Demonstrate Mo-recovery from the irradiated solution within hours after end of irradiation.
- Produce 2 Ci of Mo-99 for shipment to Covidien for testing in Tc-99m generators.

To perform these experiments, we have developed the experimental setup the flow diagram of which is shown on fig. 1. There are four experimental areas —the shielded box, glovebox area, bench top, gas analysis and gas collection systems. The shielded cell will contain the convertor/solution-target, recombiner and condensers, and the Mo-recovery column.

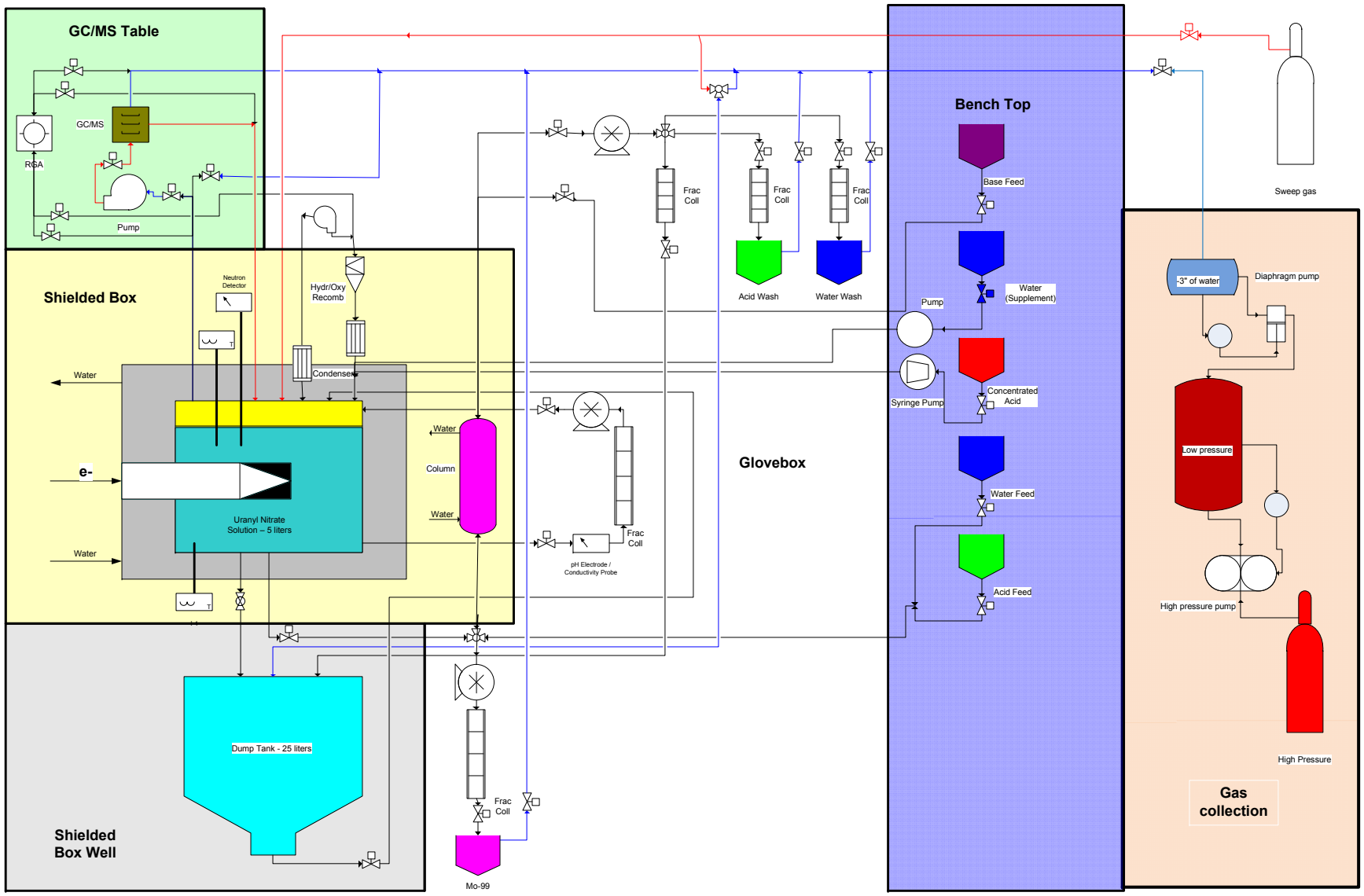

Figure 1. Schematic of the mini-SHINE/MIPS Experiment

Shielded cell

Mini-SHINE/MIPS experiment will create significant radiation field around the target during irradiation and for a long time after fission has stopped. To prevent excessive activation of the irradiation room during irradiation and to allow access to the experiment shortly after irradiation to perform separation and purification of Mo-99 we have built a lead-shielded containment cell. The expected radiation fields during irradiation are shown on Figure 2. As one can see lead shielded cell significantly decrease radiation field in the room reducing the activation of the equipment.

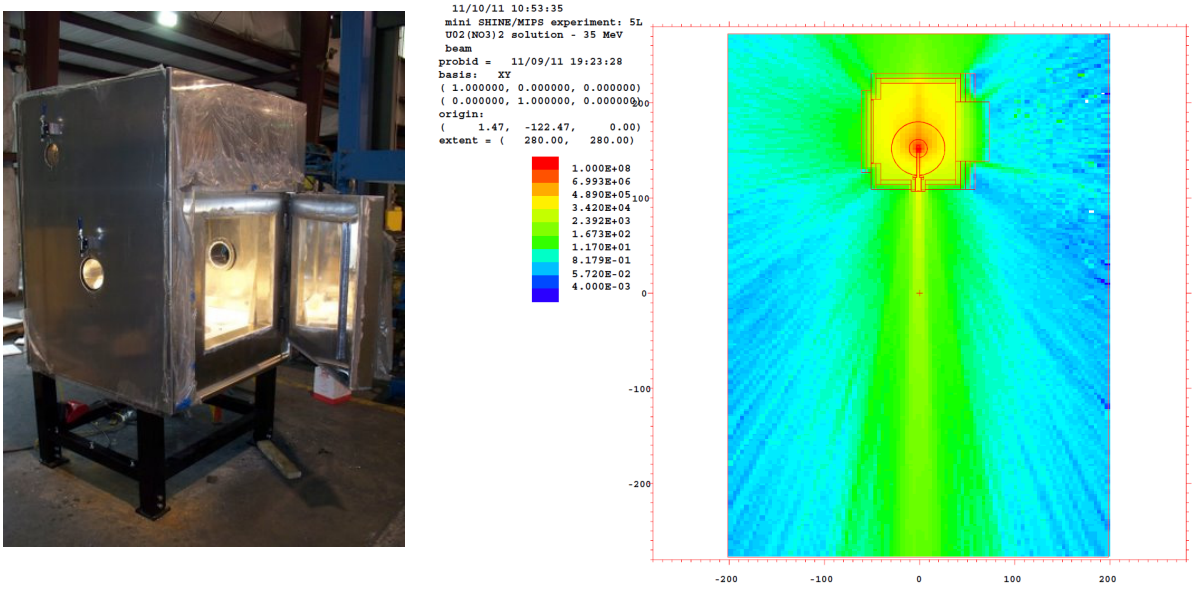

Figure 2. Shielded cell and the radiation levels in the room during mini-SHINE/MIPS experiments. Utilization of the lead shielded containment cell significantly decreases the radiation field in the room and activation of the equipment.

The electron beam enters the left side of the shielded box and strikes the convertor. The neutrons and x-rays from the convertor cause fission in the aqueous solution. Figure 3 is a detailed representation of the target assembly and shows the cooling/reflector region surrounding the target solution, penetrations for temperature probes and neutron detector in the solution, and the condensers at the top of the target-solution tank. The only valve in the shielded cell is a manual valve to dump the solution into a container in a shielded well in the case of equipment failure.

Hydrogen/oxygen recombiner

The solution is expected to generate ~75 mL/min of radiolytic gases at 0.2 kW fission power. A condenser will be situated before and after the recombiner to remove the bulk of the water vapor from the gas stream. A diaphragm pump will be used to create a high flow rate through the system. The recombiner is a Pt/Pd on alumina honeycomb catalyst, which was supplied by the Ford Motor Company. The open design of the catalyst will also allow it to handle the expected flow rates (1-12 L/min). The CSE catalyst group has successfully tested the catalyst at full-scale hydrogen/oxygen flows expected in mini-SHINE/MIPS experiments. Modeling of the main irradiation volume and plenum is also underway to determine the required flow rate to dilute the hydrogen gas sufficiently. This model is also capable of determining the amount of dead volume

in the plenum that may accumulate an explosive amount of radiolytic gases. The off-gas will be recycled in a closed-loop gas system during the experiment and will be discussed below. The recombiner and the condensers will be inside the shielded box; however, because of its size, the pump will be placed outside in a separate containment box.

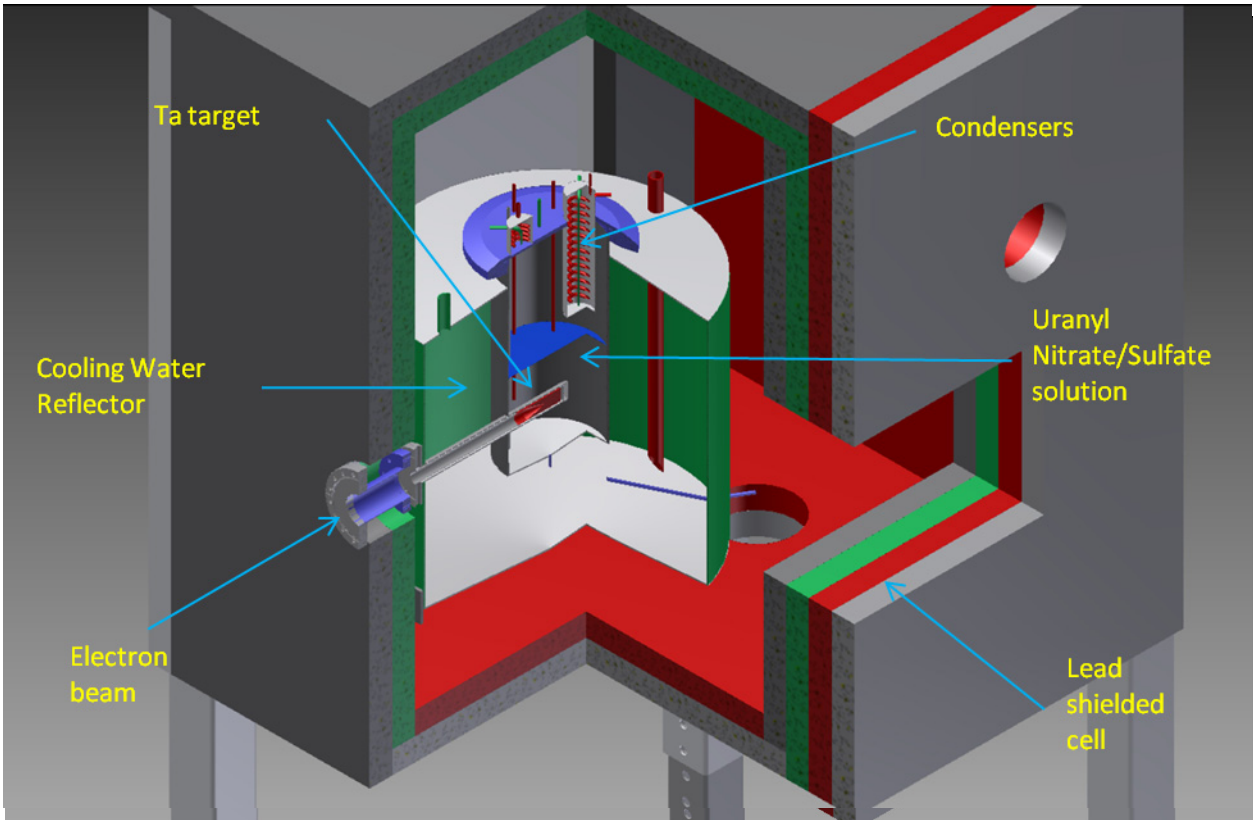

Figure 3. Detailed cross section of the target.

Photoneutron source simulations

Extensive MCNPX simulations studies have been performed to model and optimize the photoneutron target that drives the mini-SHINE/MIPS system. MCNPX is a general purpose particle transport Monte Carlo code developed by the Los Alamos National Laboratory [2] was used for calculations.

A set of simulations were performed at 20, 30, 40, 50 and 60 MeV beam energies for two different photoneutron target materials to observe photoneutron yield dependences on electron beam energy. Tantalum and DU were chosen as photoneutron target materials. Tantalum is favorable because of high-Z, high photoneutron cross-section, extremely high melting point, high chemical stability and good machinability. DU has inferior mechanical properties, but provides higher photoneutron yield due to photofission. The goal of this particular set of simulations was to compare photoneutron yields of these two materials at different energies. Summarized results are presented in Figure 4.

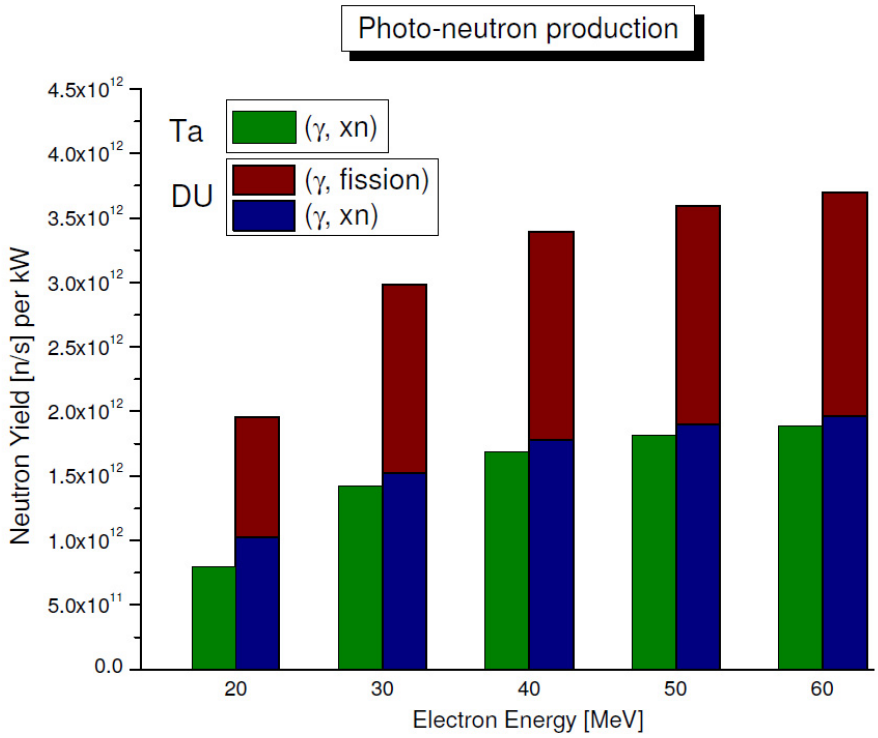

Figure 4. Dependence of photoneutorn yields normalized per kW of beam power for Ta and DU targets on electron beam energy simulated with MCNPX using ENDF/B-VII photonuclear library.

Results of the calculations clearly show that DU provides higher neutron yield due to added neurons from photofission. Neutron yield for DU target is about 2.4 times higher than that for tantalum. This is consistent to the ratio of the peak neutron production cross-sections (1.2 b/500 mb) according to ENDF/B-VII. Although DU has a significant advantage in terms of neutron yields, tantalum has superior engineering properties. Tantalum is also easier to handle after irradiation, because of radioactive photofission products in DU. Figure 4 also suggests that per kW of beam power neutron yield tends to saturate with energy. The plot shows that above 35-40 MeV there is only a marginal gain in production. Considering load curves of a ANL electron linac the optimal energy for mini-SHINE/MIPS experiments would be around 35 MeV.

For mini-MIPS/SHINE experiments a linear accelerator (linac) will drive a photo-neutron source that induces fissions in a uranyl nitrate solution surrounding the neutron target. Figure 5 below demonstrates mini-MIPS/SHINE experimental setup modeled in MCNPX. The electron beam from the linac strikes the tantalum photo-neutron target, which sits in the middle of the solution cylinder. Electrons are slowed down in the target producing bremsstrahlung photons, which in turn knocks out neutrons from the target nuclei, via(γ, xn) reactions (predominantly (γ, n)). These photo-nuclear reactions occur in the Giant Dipole Resonance (GDR) region, typically in the range of 12-16 MeV. Tantalum has engineering and handling advantages and it was chosen for the phase 1 of the mini-MIPS experiments. The conical cut in the middle of target provides gradual heat deposition that makes the target easier to cool.

The purpose of simulations described here was to estimate fission rates and fission power density in the solution. Then using materials and fluxes from MCNPX as an input for Code System for Actinide Transmutation Calculations (CINDER), the buildup and decay of the produced isotopes, including Mo-99 were calculated. The simulation model assumed an 18 MeV and 6 mm FWHM electron beam. The uranyl nitrate solution contained 145 g-U/L (20% U-235). The volume of the solution was 5 L, and it was surrounded by a water reflector tank to reflect the scattered neutrons back into the solution and increase the fission yield. The fission rate per cm^3 in the solution is shown in Figure 6 and the main results of the simulation are summarized in Table 1.

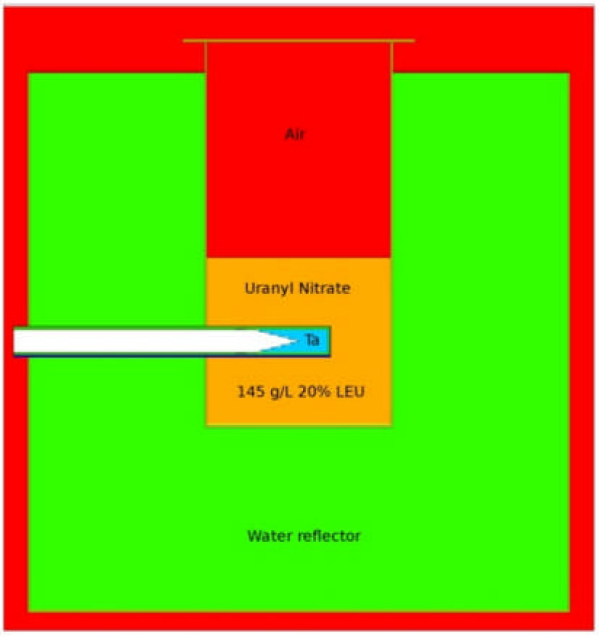

Figure 5. MCNPX geometry model of mini-MIPS/SHINE experiments.

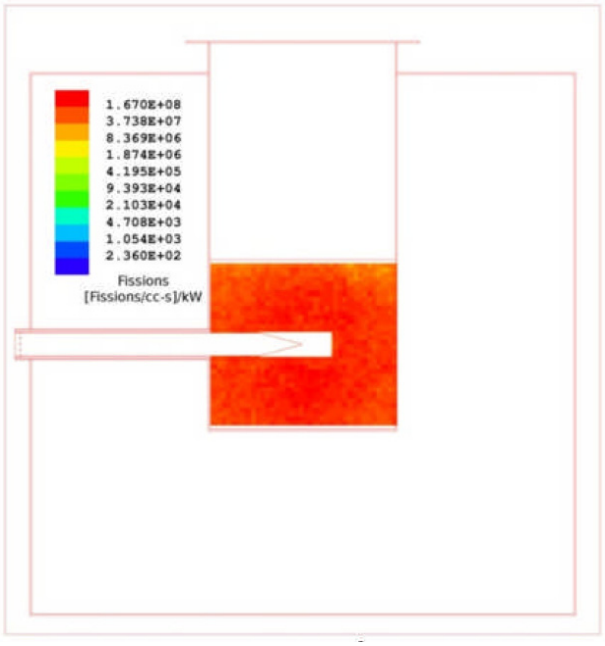

Figure 6. Fission rate per unit volume [Fission/cm^3-s] normalized per 1 kW of electron beam at 18 MeV simulated with MCNPX.

Table 1. Summary of MCNPX fission results in a 5 L uranyl nitrate solution at 18 MeV electron beam energy.

Fissions/e	9.65E-04
e/s per kW at 18 MeV	3.47E+14
Fissions/s per kW	3.35E+11
Total Fission Power [W]/kW	10.7
Average Fission Power Density [W/L]/kW	2.1

The results showed that in a 5 L uranyl nitrate solution the fission rate of 3.35E+11 fissions/s is achieved at 18 MeV per 1 kW of beam power. This is equivalent to about 10.7 W/kW of fission power and 2.1 W/L/kW of average fission power density. Experimentally, it's feasible to deliver 10 kW beam power to the target, which would result in 21 W/L average fission power density. MCNPX also provided other useful information such as power deposition in different parts of the geometry and spatial distributions of electron, photon, and neutron fluxes. The neutron flux as a function of neutron energy was also generated from this run.

The next step in the calculation was to provide the MCNPX geometry model and obtained the neutron flux in the solution as an input to an isotope transmutation code called CINDER in order to handle build up and decay of isotope inventory and figure out the end of bombardment activity of Mo-99. For CINDER calculations we assumed 10 kW beam power and 40 hour irradiation time. Isotope activities were reported at the end of the run and also at 1 hour, 8 hour, 1 day, 3 day, 1 week, 2 week, 3week, and 4 week time intervals. Resulting Mo-99 activity is presented in Figure 7.

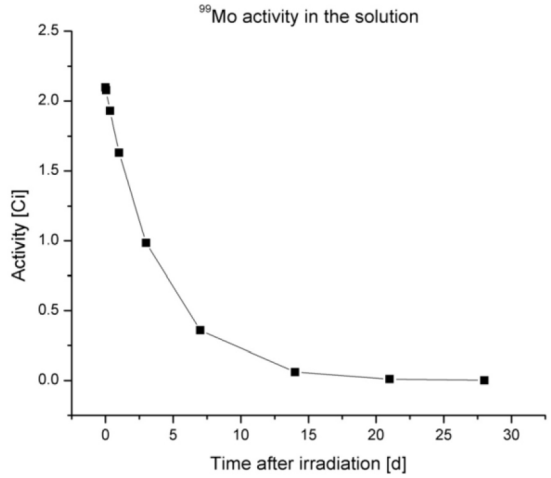

Figure 7. End-of-run and decay activities [Ci] of Mo-99 as a result of 40 hour irradiation with 10 kW beam power at 18 MeV obtained from CINDER.

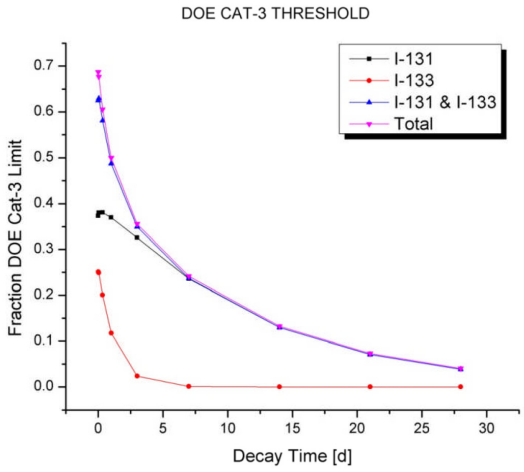

Figure 8. CINDER results for DOE category-3 thresholds for I-131, I-133 and all of the
isotopes combined as a function of time after the irradiation.

The plot shows about 2.1 Ci of Mo-99 will be produced after 40 hours of irradiation with 10 kW beam power at 18 MeV. This amount of activity is high enough to test the separation and recovery of Mo-99 in the presence of all other fission products. CINDER also reported fractions of the DOE category-3 thresholds for each isotope. Calculations show that all the produced isotopes combined make up around 70% of the category-3 limit at the end of irradiation and decay rapidly thereafter. It drops below 10% category-3 limit three weeks after the irradiation is complete.

The main contributors to the category-3 limit fraction are two isotopes – I-131 and I-133. These two isotopes together define the total category-3 fraction almost entirely. Figure 8 shows the category-3 threshold fractions for I-131 and I-133 (separately and together) and all the isotopes

combined from the CINDER calculations. This result demonstrates that we can run full scale irradiation every four weeks without exceeding category-3 threshold for radioisotope inventory.

Gas analysis system
Gas samples will be collected both from the head space above the target solution and above the catalytic convertor. Both a GC/MS (gas chromatograph with a mass spectrometry detector) and RGA (residual gas analyzer) will be used to measure the composition and generation rate of radiolytic gases. RGA will be used for real time monitoring of the gas composition for major gasses, while GC/MS will be periodically used to monitor low concentration off-gas components.

Closed loop solution monitoring system
During irradiation, a small volume of the solution will also be pumped through a closed-loop system, which will be set up in a glovebox next to the shielded cell (Figure 6). In the closed system, pH, conductivity, and turbidity will also be monitored continually. The radiation stability of these components is now being tested at the Van de Graaff electron accelerator. A sampling system, using syringes and gear motors, will collect timed samples during the run. The line and samples will be shielded so samples can be removed after irradiation for further investigation. We will have the ability to add acid and water to the target solution during operation if increases in the pH or conductivity are observed (bottom right of Figure 1). The ability to control pH during operation of the MIPS is one of the parameters we would like to explore in these experiments.

Separation system
The Mo-recovery column is also located in the shielded cell. A second glovebox will house the sampling stations (fraction collectors), and cold feeds will be added from a bench-top station (Figure 1.). A few hours after the end of irradiation, the target solution will be passed through the titania column to recovery Mo from the irradiated solution. A fraction of radioiodine and minor amounts of other fission and activation products will also be captured. Small samples of the effluent will be collected, and the bulk of the solution will be passed into the shielded volume below the shielded box. The column will then be washed first with dilute nitric or sulfuric acid and then with a water wash. Small fractions of these effluents will also be collected for later analysis. The spent wash solutions will be returned to the glovebox. All these solutions will be passed through the column in the up-flow direction. The strip solution will be 1 M ammonium hydroxide; it to will be run in the down-flow direction, sampled periodically, and kept in the glovebox. All sampling stations and collection vessels will be shielded. Mock ups are being prepared and tested for all operations.

Mo-99 purification
At the end of the recovery operation, the Mo-product will be removed from the glovebox in the linac target room and moved to a glovebox in the adjacent room. In this glovebox, the ammonia and water will be evaporated using a rotovap. Nitric acid will be added to the dry residue and also evaporated to dryness. The rotovap is a closed system. A NaOH scrubber will be between the rotovap and the vacuum pump to trap any iodine vapors that might escape the condenser flask. This process will remove almost all the radioiodine from the solution and allow the Mo residue to be transferred to radiological laboratory for purification. Early irradiations will

produce minor amounts of fission products, so the Mo can be purified in a hood. When two Ci of Mo-99 are produced, the purification will be performed in the ANL Junior Cave.

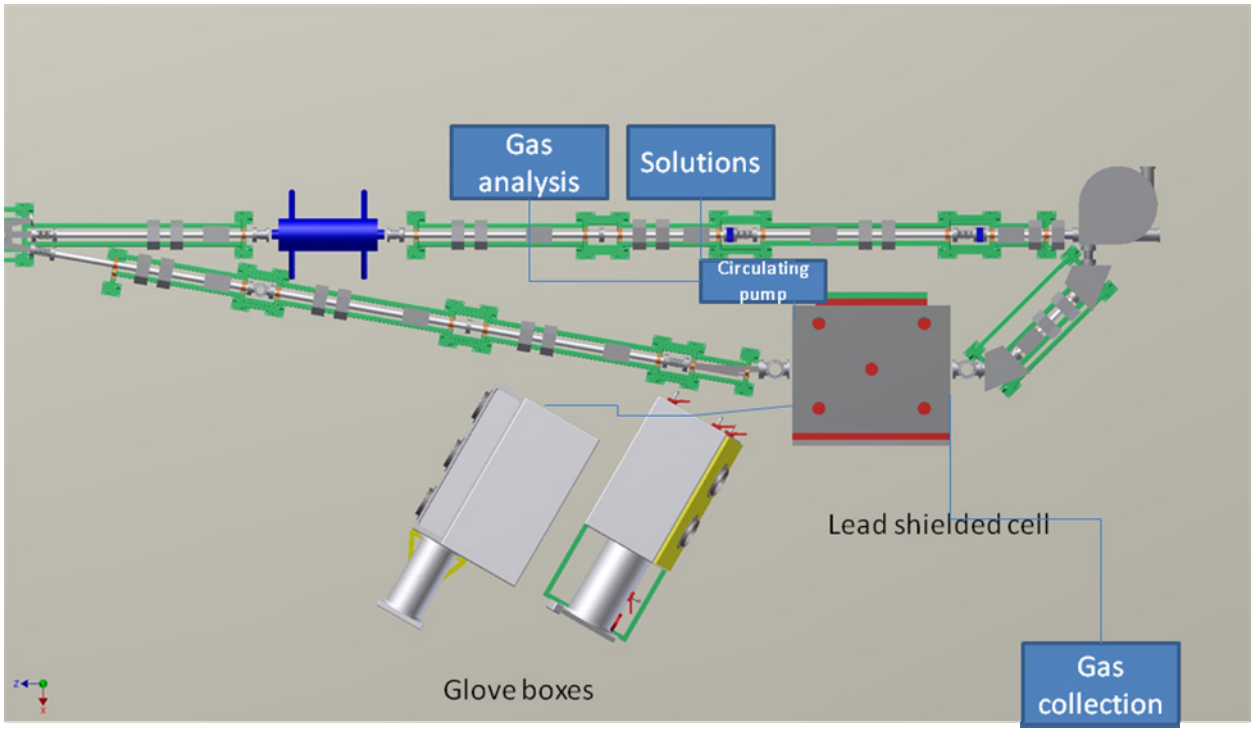

Figure 9. Mini-SHINE/MIPS setup in irradiation room (top veiw).

Gas collection system

During operation, the off gas is contained in a closed-loop/recycle system. The negative pressure in the system during irradiation and separation will be maintained using the 3-tank/2-pump system shown on the right side of Figure 1. At the end of operation, the off gas will be evacuated into a tank for decay storage. The gas will need to be stored in the tank for about 3 months to allow the short-lived Xe and I radioisotopes to decay.

3. Schedule for the Mini-SHINE/MIPS Experiments

The schedules for mini-SHINE/MIPS are phased approaches in three ways. Phase-1 is a prelude to the higher power densities required in Phase-2. Further, both phases are scheduled to go through a schedule of less to more complex experiments, and these experiments will be run through a series of increasing power and time irradiations to reach the final objectives. Initial experiments will be run using only water as the target solution; gamma radiolysis will produce hydrogen and oxygen only and will test the catalytic convertor, the gas-recycle loop, off-gas-collection system, the off-gas monitoring system, the solution sampling loop, and internal target solution thermocouples and cooling loop.

Once these operations have been tested, the target solution will be changed to sodium-nitrate and then sodium sulfate solutions. This will allow testing of the solution-monitoring systems as well as the previously tested systems.

Once operations of all systems are verified, a uranyl-nitrate solution will be irradiated. Short times and power runs will allow us to test the Mo-recovery column operations. Following successful experiments with the uranyl-nitrate system, uranyl sulfate solutions will be used as the target solutions.

Phase 1 experiments (5 liter target solutions, Ta converter, 10 kW beam power) are schedule to begin in December 2011. Phase-2 will begin after completion of the phase 1 experiments and once all systems have been tested under phase-2 conditions (20 liter solution, DU converter, up to 30 kW beam power). We plan to start phase 2 experiments in July 2012.

4. Conclusion

- In this work we have presented design of the mini-SHINE/MIPS experiments planned at the linac facility of Argonne National Laboratory.
- We have discussed all major subsystems of the experiments and what data we will collect during the experiment.
- We have presented results of the computer simulations of the photoneutron target and neutron fission of the solution. Those result shows that we can generate sufficient amount of Mo-99 isotope and other fission products to study gas evolution, chemistry of the solution and demonstrate separation process.
- We are planning to start phase-1 mini-SHINE/MIPS experiments in December 2011 and phase-2 experiments in September 2012.

5. Acknowledgement

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