Overview: Argonne Assistance in Developing SHINE Production of Mo-99


Argonne National Laboratory

Mo-99 Topical Meeting
Washington DC
June 24-27, 2014
Potential Domestic Mo-99 Producer

- SHINE Medical Technologies
- D/T-accelerator-driven process
- LEU uranyl-sulfate solution

- Titania sorbents to separate and recover Mo-99
- LEU-Modified Cintichem process for purification
- Sulfate-to-nitrate conversion followed by UREX for clean-up – Contactor design
- Bubble formation - thermal hydraulic effects
- Potential precipitate formation

Mini-SHINE Experiments
Mini-SHINE Experiments

- Argonne’s mini-SHINE experiment will irradiate aqueous uranyl-sulfate solutions using an electron linac to:
  - Study the effects of fission on target-solution chemistry and radiolytic off-gas generation
  - Demonstrate the recovery and purification of Mo-99 from an irradiated target solution
  - With the assistance of PNNL, sample off gas for Xe, Kr, and I
  - Monitor pH, conductivity, and turbidity during irradiation

Phase 1
- Linac will be operated initially at 35 MeV and 10 kW beam power on the target
- 5 L solution will be irradiated with neutrons generated through gamma-n reaction in tantalum target
- The maximum solution power will be ≤ 0.05 kW/L
- Up to 2 Ci of Mo-99 will be produced

Phase 2
- Experiment will be conducted at 35 MeV beam energy and up to 30 kW beam power
- 20 L solution will be irradiated with neutrons generated in a depleted-uranium (DU) target
- The maximum solution power will be ≤ 0.5 kW/L
- Up to 20 Ci of Mo-99 will be produced
Mini-SHINE Progress

- **Phase 1**
  - Conservative approach
    - Irradiation of water, followed by sodium-bisulfate solutions, followed by uranyl-sulfate solutions
    - To verify all system components before producing fission products
  - Radiation stability of components verified using Van de Graaff
  - Water irradiations completed
  - Sodium bisulfate irradiations near completion – corrosion slowed progress
  - Uranyl sulfate irradiations performed after final long NaHSO$_4$ irradiation

- **Phase 2**
  - Equipment has been fabricated
  - DU target fabrication near completion
  - Experiments to begin after phase 1
Mini-SHINE Experiment Flow Diagram
5 L Solution Irradiation Vessel

- 5 L uranyl sulfate solution in a 304SS vessel
- Large access port for gas analysis, flow loop, thermocouple, neutron-flux monitor, etc.
- 15-cm light-water reflector/cooler

- Test of the target, gas analysis, recombiner and gas collection system using pure water was successfully performed in April 2012
Target Solution Monitoring Glovebox

- pH, conductivity, and turbidity measured during irradiation – done remotely
- Up to 15 samples collected during irradiation – done remotely but retrieved manually
- No significant changes in pH, conductivity or turbidity during NaHSO$_4$ irradiations
- FeSO$_4$ added to decrease peroxide formation
Mo-Recovery Glovebox

- Titania column to capture Mo-99 from irradiated uranium solution
- All operations are done remotely
  - Processing will begin 0-10 hours following irradiation
  - Target solution will be fed from the irradiation tank
  - Column effluent will go to the dump tank below the hot cell
  - Cold feeds are located inside the glovebox
  - Mo-product will exit the glovebox into a shielded cask
- Up to 45 samples can be collected from the feed, washes, and strip effluents
- Mo-product will be transferred to second hot cell as early as possible
Concentration Column and LEU-Modified Cintichem

- In a second shielded cell (bigfoot), the Mo-product solution will be concentrated by a factor of ~15 using a much smaller column
  - Mo-product from the second column will then be acidified for entry into the LEU Cintichem process
  - Mo product will be concentrated down to 50 mL
  - LEU-Modified Cintichem process will be used to purify Mo-product
**NaHSO₄ Experimental Results**

- Blue-colored solutions observed after contacting SS components in mini-SHINE setup
- Series of corrosion tests performed – NaHSO₄ most corrosive – 0.5 mm/yr after 30 days
- UO₂SO₄ – 0.05 mm/yr after 30 days
- Low %Mo recovered after 1st column – adsorption or plating out in system
- NaHSO₄ – more corrosive – ultimate goal – UO₂SO₄

<table>
<thead>
<tr>
<th>Date of Experiment</th>
<th>Irradiation</th>
<th>Irradiation Time (min)</th>
<th>1st Column</th>
<th>2nd Column</th>
<th>Cintichem</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/3/2014</td>
<td>no</td>
<td>NA</td>
<td>80%</td>
<td>88%</td>
<td>84%</td>
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<tr>
<td>3/10/2014</td>
<td>no</td>
<td>NA</td>
<td>88%</td>
<td>96%</td>
<td>62%</td>
</tr>
<tr>
<td>3/26/2014</td>
<td>yes</td>
<td>80</td>
<td>48%</td>
<td>82%</td>
<td>64%*</td>
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<tr>
<td>4/15/2014</td>
<td>yes</td>
<td>300</td>
<td>80%</td>
<td>95%</td>
<td>70%**</td>
</tr>
</tbody>
</table>

* % Mo recovered after evaporation – Mo-product bottle broke; ** % Mo recovered after evaporation and LEU-Modified Cintichem
Gas Analysis System
Off-Gas Recovery System

- All off-gases from experiment will be collected and decay stored.
- Three cylinder system with increasing pressure: <0=>4.5=>3500 psig
- Automatically maintain pressure in the solution vessel at -3 inches of water.
- Final storage 6000 psig cylinder.
- Pumps inside vessels to prevent pumps leaking into atmosphere.
Off-Gas Sampler for Gamma Counting of Fission Gases

- Collect 15 100 mL samples
  - Vacuum in canisters will draw sample
  - Can collect up to 15 time points using 16 port valve
  - 24 V valve is used to start and stop sample collection
  - Valves are controlled remotely
- Samples will be shipped to PNNL for gamma counting
Gas Analysis Results

- Results from run on 04/15/14
- More shielding added around RGA
- New condenser added to minimize liquid in the system
- Catalytic recombiner wrapped with heat tape
- Analog outputs added to RGA
Contactor Design for Cleanup

- Target solution cleanup done every 4 or more irradiation cycles
- Sulfate-to-nitrate conversion – mixture of $\text{Ba(NO}_3\text{)}_2$ and $\text{Sr(NO}_3\text{)}_2$
- UREX - current means of cleanup
- Contactor size – important decision for SHINE
- V-2, V-3.5, & V-5 considered
  - V-2 and V-5 are currently commercially available from CINC
  - If V-3.5 chosen, Argonne to design and work with CINC for fabrication
- Startup, rinse, and shutdown times comparable, but hold-up volumes are proportional to the rotor diameter to the third power
- Process time, waste volumes, and space – determining factors
- 260 L batch
- V-3.5 – being pursued

<table>
<thead>
<tr>
<th>Contactor Size</th>
<th>Flow Rate (L/min)</th>
<th>Process Time (hr)</th>
<th>Foot print – 30 stages (m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-2</td>
<td>1</td>
<td>19</td>
<td>1.6</td>
</tr>
<tr>
<td>V-3.5</td>
<td>5</td>
<td>5.7</td>
<td>2.0</td>
</tr>
<tr>
<td>V-5</td>
<td>15</td>
<td>3</td>
<td>2.8</td>
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</table>
Waste Optimization

- Target solution cleanup – majority of SHINE’s waste
- Separation, recovery, and purification – another portion
- Equipment and other components – dependent on replacement frequency
- SHINE process flowsheets reviewed
- Partitioning of components for various steps – based on chemistry developed at Argonne
- Best ways to eliminate GTCC
- Ongoing study with final report available in September
Bubble Experiments

- Results from mini-scale bubble experiments at Van de Graaff – NaHSO₄

- Study thermal hydraulics of sector of SHINE target solution vessel
- High radiation field from electron beam of linac
- Data can be used to validate computer models for bubble formation
- 20 L depleted uranyl-sulfate solution
- Irradiations expected to begin July 2014
The Geochemist’s Workbench® was used to model SHINE target solution—predicted compounds that may precipitate and needed experimental study.

Table above shows concentration when precipitation occurred and amount of time elapsed before it was observed.

- ZrO$_2$, SnO$_2$, BaSO$_4$, CoWO$_4$, and RuO$_2$ – unknown precipitation kinetics
- Potential precipitates were added as salts to 140 g-U/L UO$_2$SO$_4$ solutions
- Experiments done at RT and 80°C at concentrations up to 30 mM except Ru – only 0.5 mM
- Solutions were monitored for up to 30 days

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>RT Conc. (mM)</th>
<th>60°C Conc. (mM)</th>
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<tbody>
<tr>
<td>ZrO$_2$</td>
<td>No precipitation</td>
<td>No precipitation</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>30 mM – instant 20 mM – 2 weeks</td>
<td>30 mM – instant 20 mM – 2 weeks</td>
</tr>
<tr>
<td>BaSO$_4$</td>
<td>1 mM – instant</td>
<td>1 mM – instant</td>
</tr>
<tr>
<td>CoWO$_4$</td>
<td>0.1 mM – 2 min</td>
<td>10 mM – instant 3 mM – 1.5 weeks 1 mM – 3 weeks</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>No precipitation</td>
<td>No precipitation</td>
</tr>
</tbody>
</table>
Conclusions and Future Work

- Mini-SHINE experiments with $\text{UO}_2\text{SO}_4$ to begin in next few weeks
- A few short irradiations and 1 long irradiation will be performed first
- Mo-product from 2nd long irradiation will be shipped to a Tc-99m generator manufacturer
- V-3.5 is the current choice for contactor design
- Waste optimization study is ongoing
- Bubble experiment is currently being setup at the linac
- Modeling and experimental results suggest fission product precipitation should not occur – precipitation of uranyl peroxide is a bigger concern

- Redox chemistry and iodine speciation – important data from mini-SHINE experiments
- Final waste optimization report – September 2014
- Bubble experiments – July 2014
- Uranyl peroxide – temperature- and power-controlled experiments at Van de Graaff
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