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

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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 $\leq$ 0.05 kW/L
- Up to 2 Ci of Mo-99 will be produced

Phase 2

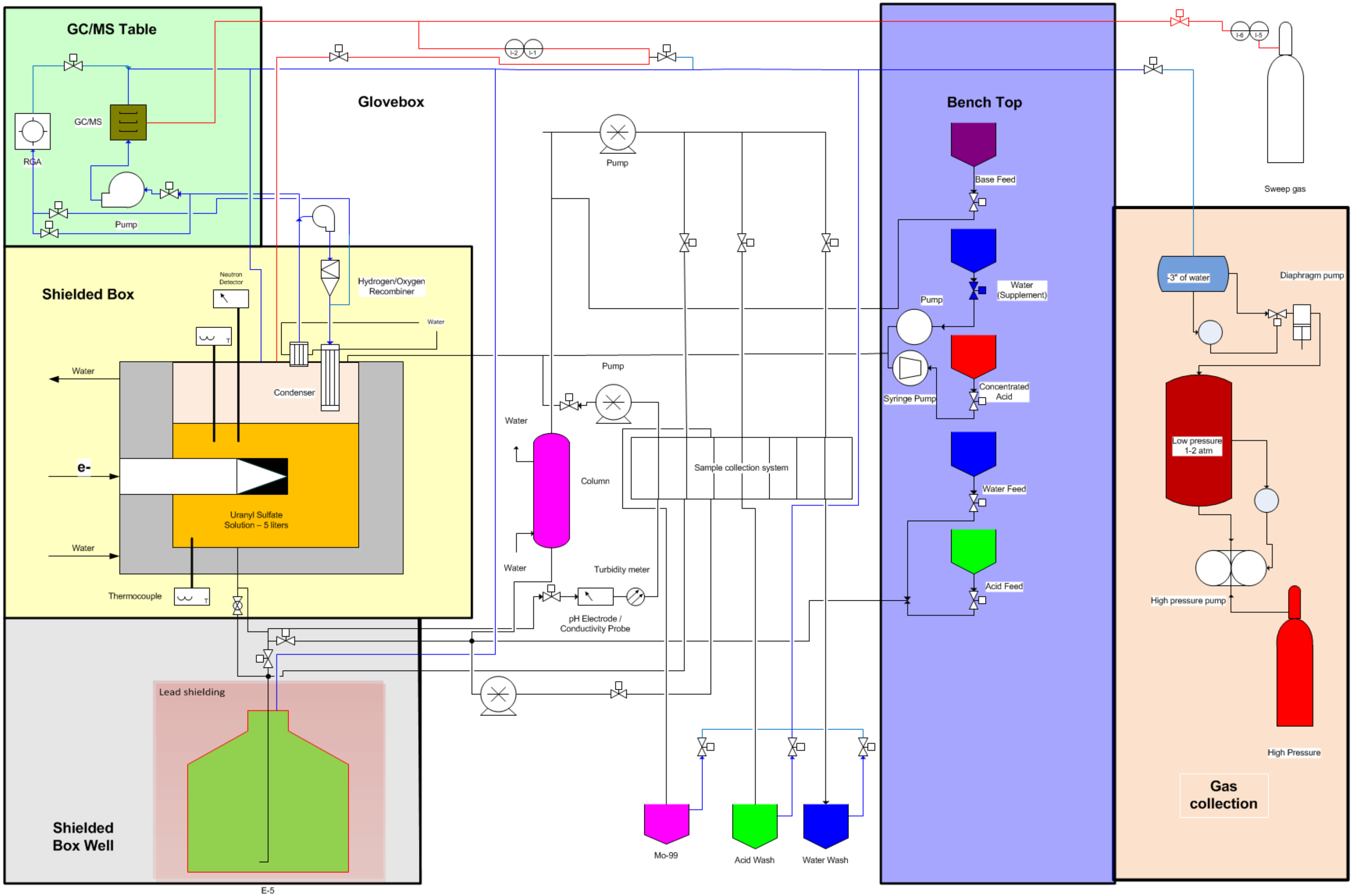
- Experiment will be conducted at 35 MeV beam energy and up to 30 kW beam power
- 20 L solution will be irradiated with neutrons generated in a depleted-uranium (DU) target
- The maximum solution power will be $\leq$ 0.5 kW/L
- Up to 20 Ci of Mo-99 will be produced

Mini-SHINE Progress

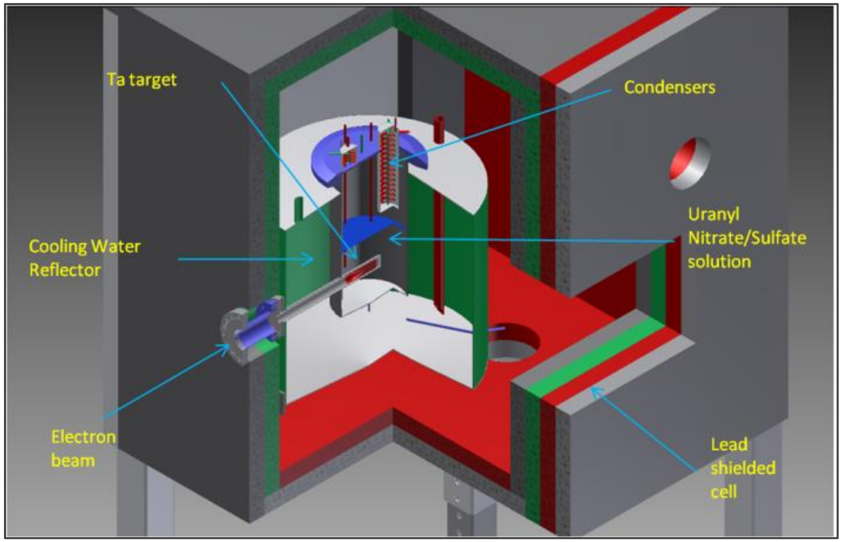
- Phase 1
  - Conservative approach
    - Irradiation of water, followed by sodium-bisulfate solutions, followed by uranyl-sulfate solutions
    - To verify all system components before producing fission products
  - Radiation stability of components verified using Van de Graaff
  - Water irradiations 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

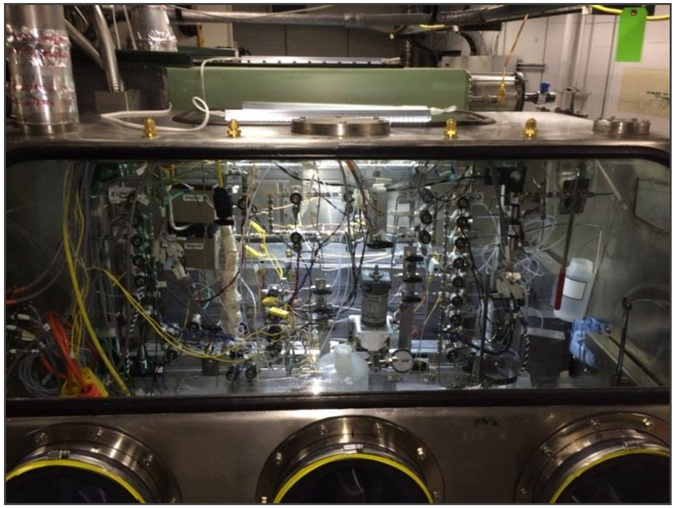
- Test of the target, gas analysis, recombiner and gas collection system using pure water was successfully performed in April 2012

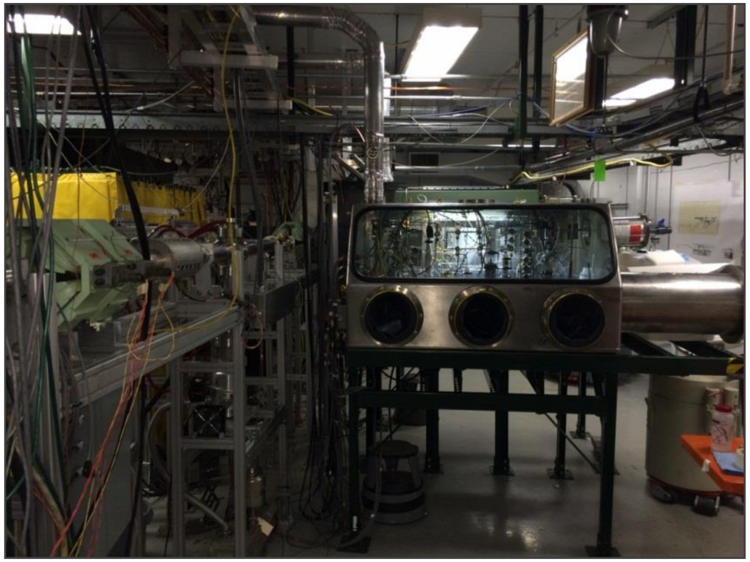
Target Solution Monitoring Glovebox

- 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

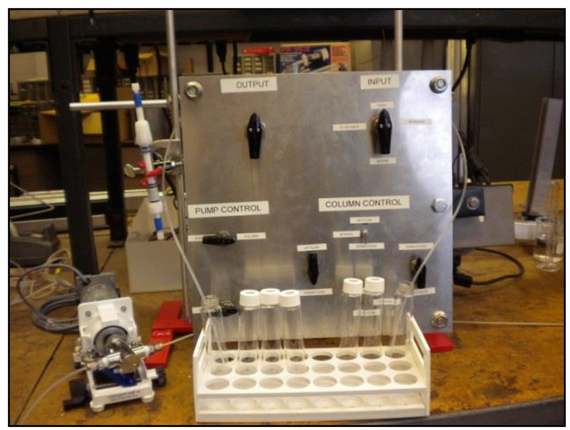
- Titania column to capture Mo-99 from irradiated uranium solution
- All operations are done remotely
  - Processing will begin 0-10 hours following irradiation
  - Target solution will be fed from the irradiation tank
  - Column effluent will go to the dump tank below the hot cell
  - Cold feeds are 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

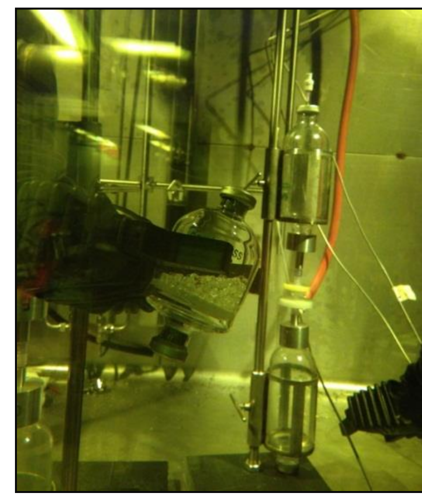




Concentration Column and LEU-Modified Cintichem

- 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





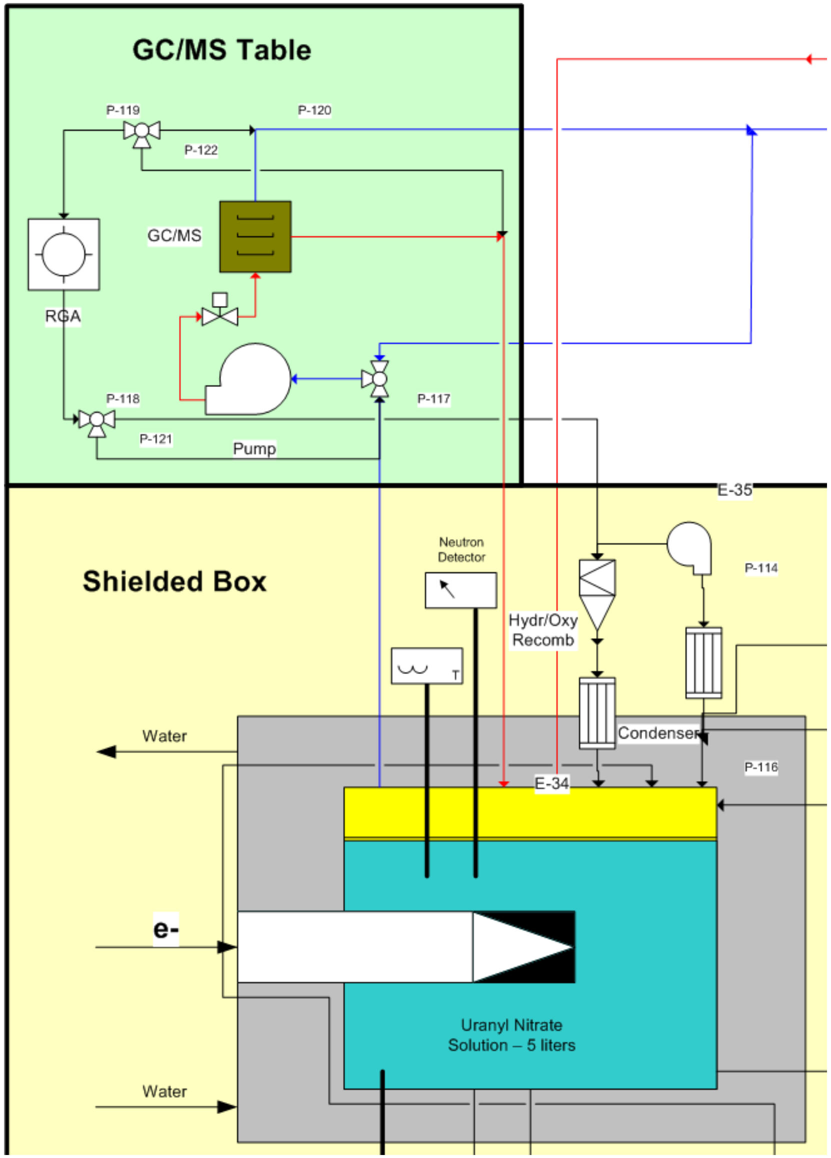
$NaHSO_4$ Experimental Results

- Blue-colored solutions observed after contacting SS components in mini-SHINE setup
- Series of corrosion tests performed – $NaHSO_4$ most corrosive – 0.5 mm/yr after 30 days
- UO_2SO_4 – 0.05 mm/yr after 30 days
- Low %Mo recovered after 1st column – adsorption or plating out in system
- $NaHSO_4$ – more corrosive – ultimate goal – UO_2SO_4

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

* % Mo recovered after evaporation – Mo-product bottle broke; ** % Mo recovered after evaporation and LEU-Modified Cintichem

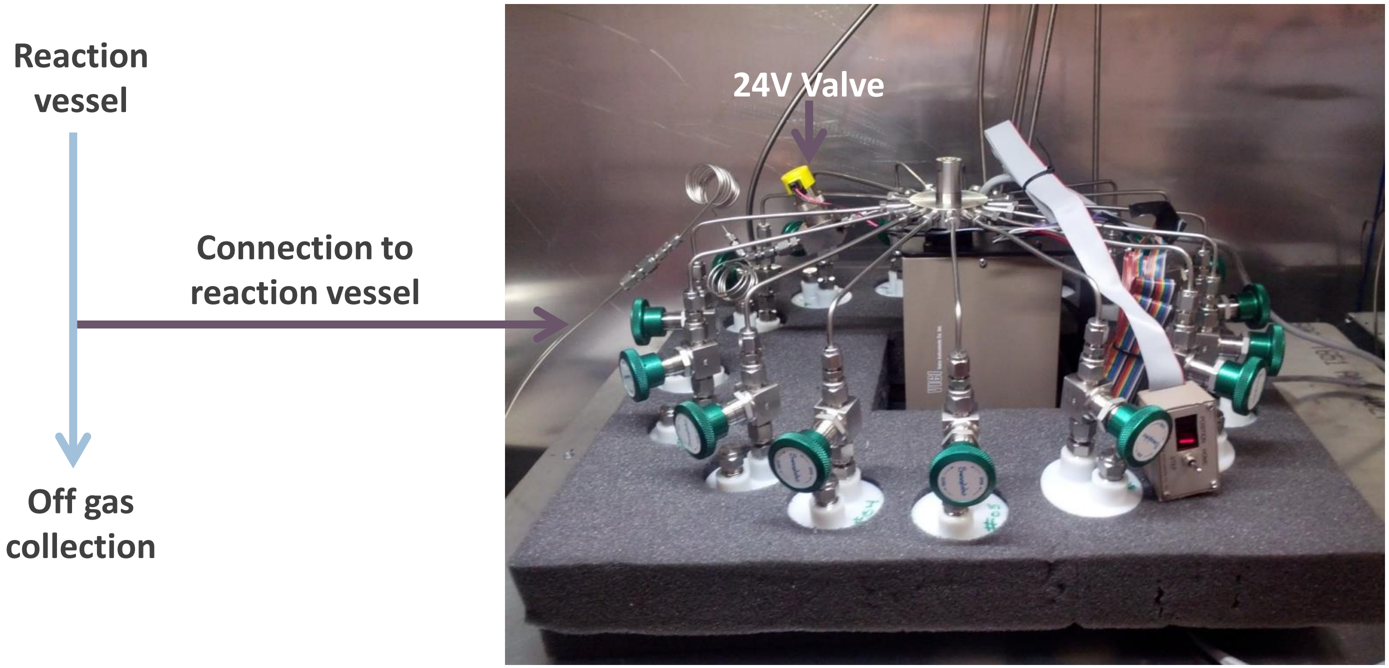
Gas Analysis System



Off-Gas Recovery System

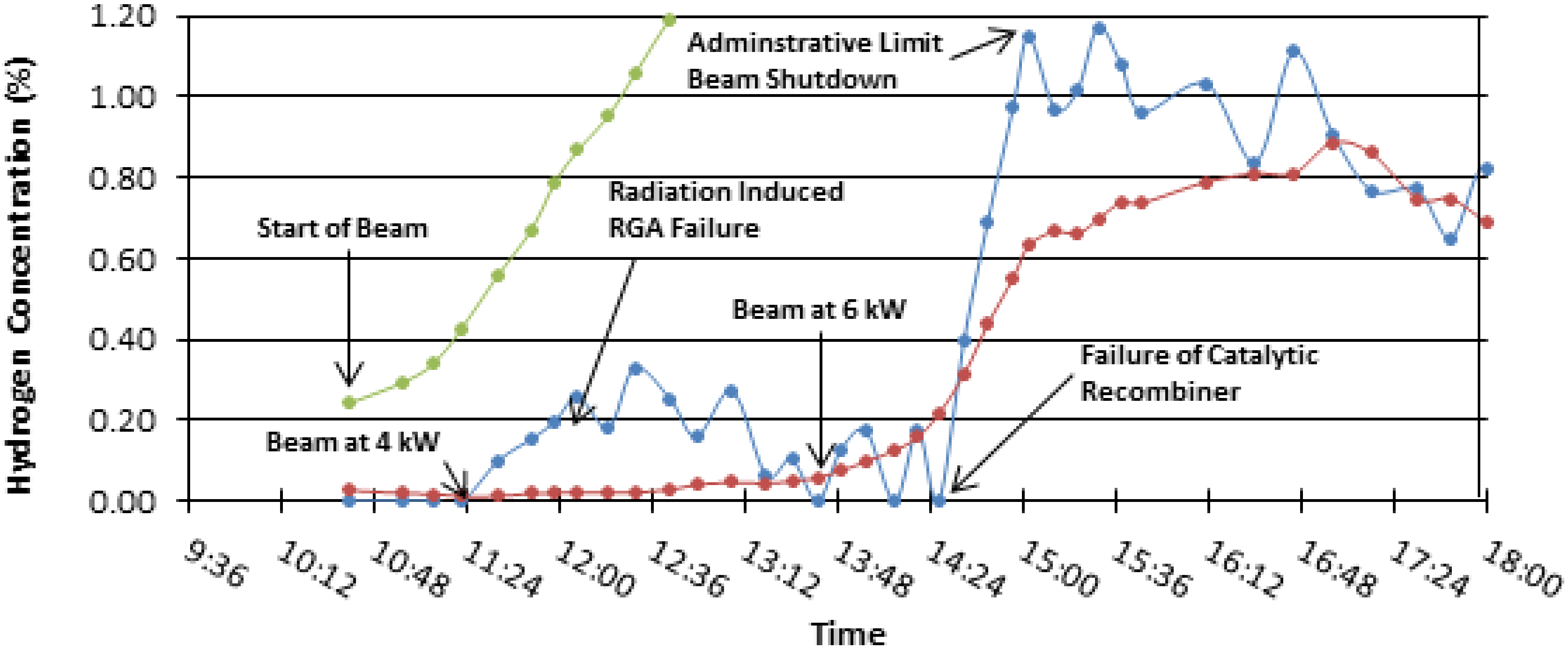
- All off- gases from experiment will be collected and decay stored
- Three cylinder system with increasing pressure <0=>4.5=>3500 psig
- Automatically maintain pressure in the solution vessel at -3 inches of water
- Final storage 6000 psig cylinder
- Pumps inside vessels to prevent pumps leaking into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

Contactor Size	Flow Rate (L/min)	Process Time (hr)	Foot print – 30 stages (m^2)
V-2	1	19	1.6
V-3.5	5	5.7	2.0
V-5	15	3	2.8

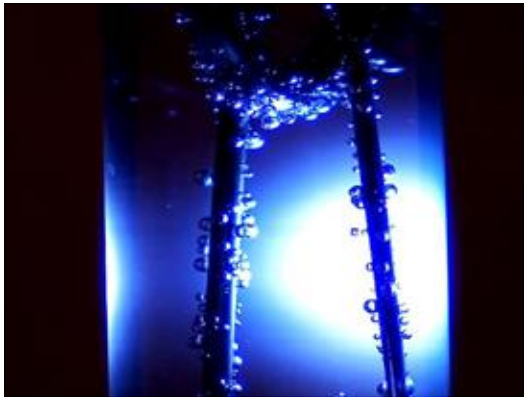
- Target solution cleanup done every 4 or more irradiation cycles
- Sulfate-to-nitrate conversion – mixture of $Ba(NO_3)_2$ and $Sr(NO_3)_2$
- UREX - current means of cleanup
- Contactor size – important decision for SHINE
- V-2, V-3.5, & V-5 considered
  - V-2 and V-5 are currently commercially available 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

Waste Optimization

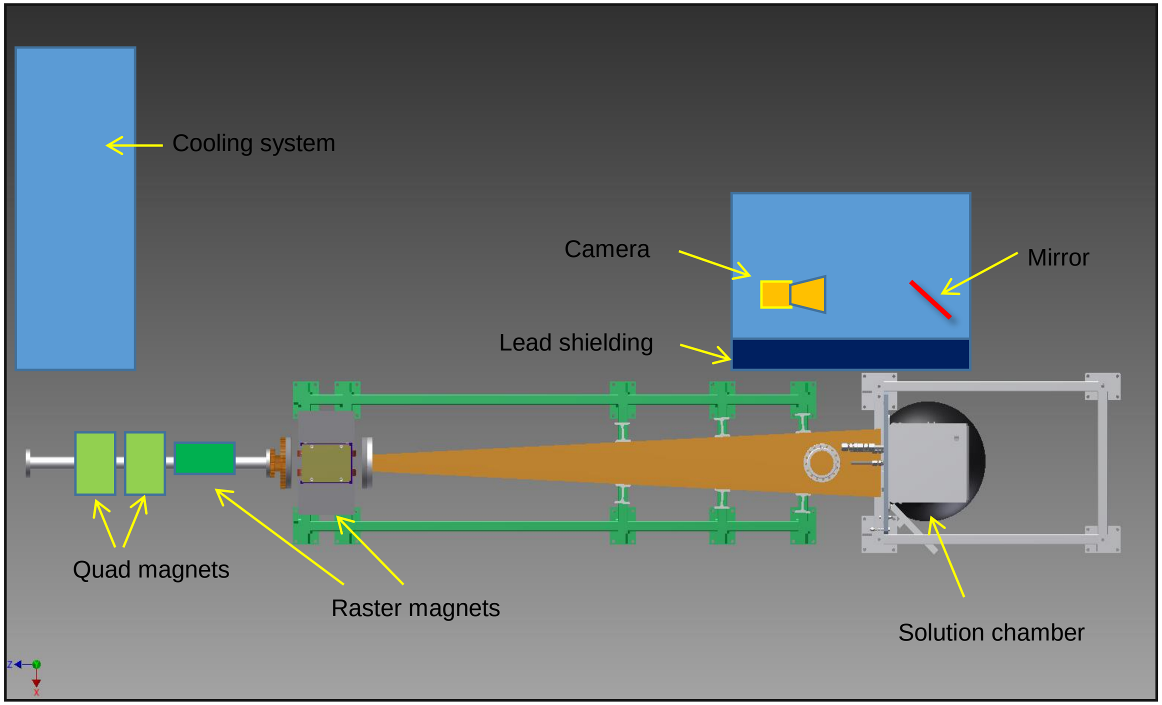
- Target solution cleanup – majority of SHINE's waste
- Separation, recovery, and purification – another portion
- Equipment and other components – dependent on replacement frequency
- SHINE process flowsheets reviewed
- Partitioning of components for various steps – based on chemistry developed at Argonne
- 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 – $NaHSO_4$



- 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



Potential Precipitates

Precipitate	RT Conc. (mM)	60°C Conc. (mM)
ZrO_2	No precipitation	No precipitation
SnO_2	30 mM – instant 20 mM – 2 weeks	30 mM – instant 20 mM – 2 weeks
$BaSO_4$	1 mM – instant	1 mM – instant
$CoWO_4$	0.1 mM – 2 min	10 mM – instant 3 mM – 1.5 weeks 1 mM – 3 weeks
RuO_2	No precipitation	No precipitation

- 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_2SO_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

Conclusions and Future Work

- Mini-SHINE experiments with UO_2SO_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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