

# Development of the Mini-SHINE/MIPS Experiments

S. Chemerisov, A. J. Youker, A. Hebden, N. Smith, P. Tkac, C. D. Jonah,  
J. Bailey, J. Krebs, V. Makarashvili, B. Micklich, M. Kalensky, S. Zaijing,  
R. Gromov, and G. F. Vandegrift  
Argonne National Laboratory

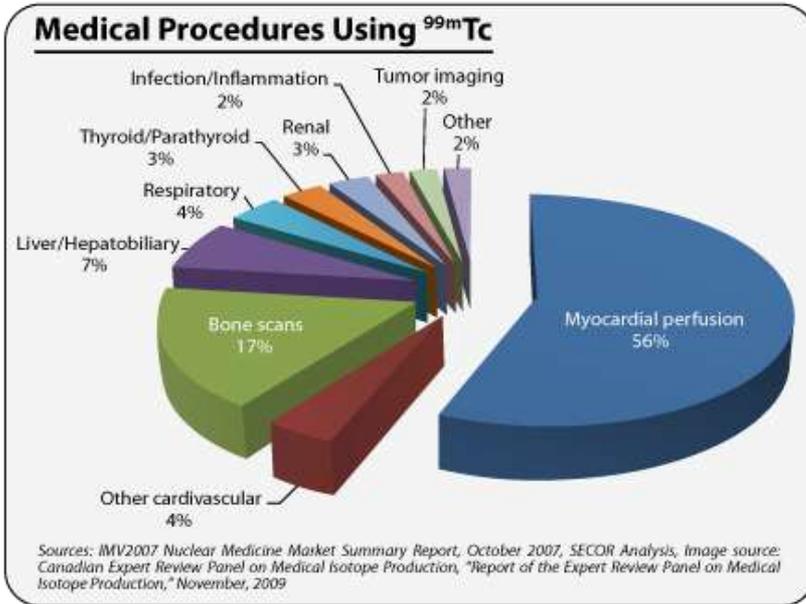
Mo-99 2013 TOPICAL MEETING

April 1-5, 2013

Embassy Suites Downtown - Lakeshore  
Chicago, Illinois

# GTRI Conversion Program

- Assisting current producers to convert from HEU targets to LEU targets for production of Mo-99
- **Accelerating the establishment of a reliable supply of commercial non-HEU-based Mo-99 in the United States**



The most common radioisotope used in diagnosis is technetium-99, with some 30 million procedures per year, accounting for 80% of all nuclear medicine procedures worldwide.

Argonne is assisting two of the potential domestic producers: Babcock and Wilcox Technical Services Group (B&W) and the 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 SHINE, which creates Mo-99 by neutron-induced fission of LEU in a subcritical aqueous solution; the neutron source is a D/T generator.

The mini-SHINE/MIPS experiments planned at Argonne Low Energy Accelerator Facility (LEAF) will provide important design data for both uranyl-sulfate and uranyl-nitrate based AHRs and target solutions.



# Mini-SHINE/MIPS Experiments

- Argonne's mini-SHINE/MIPS experiment will irradiate aqueous uranyl-sulfate and -nitrate 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  $^{99}\text{Mo}$  from the irradiated target solution
  - With the assistance of PNNL, sample off gas for Xe, Kr, and I

## Phase 1

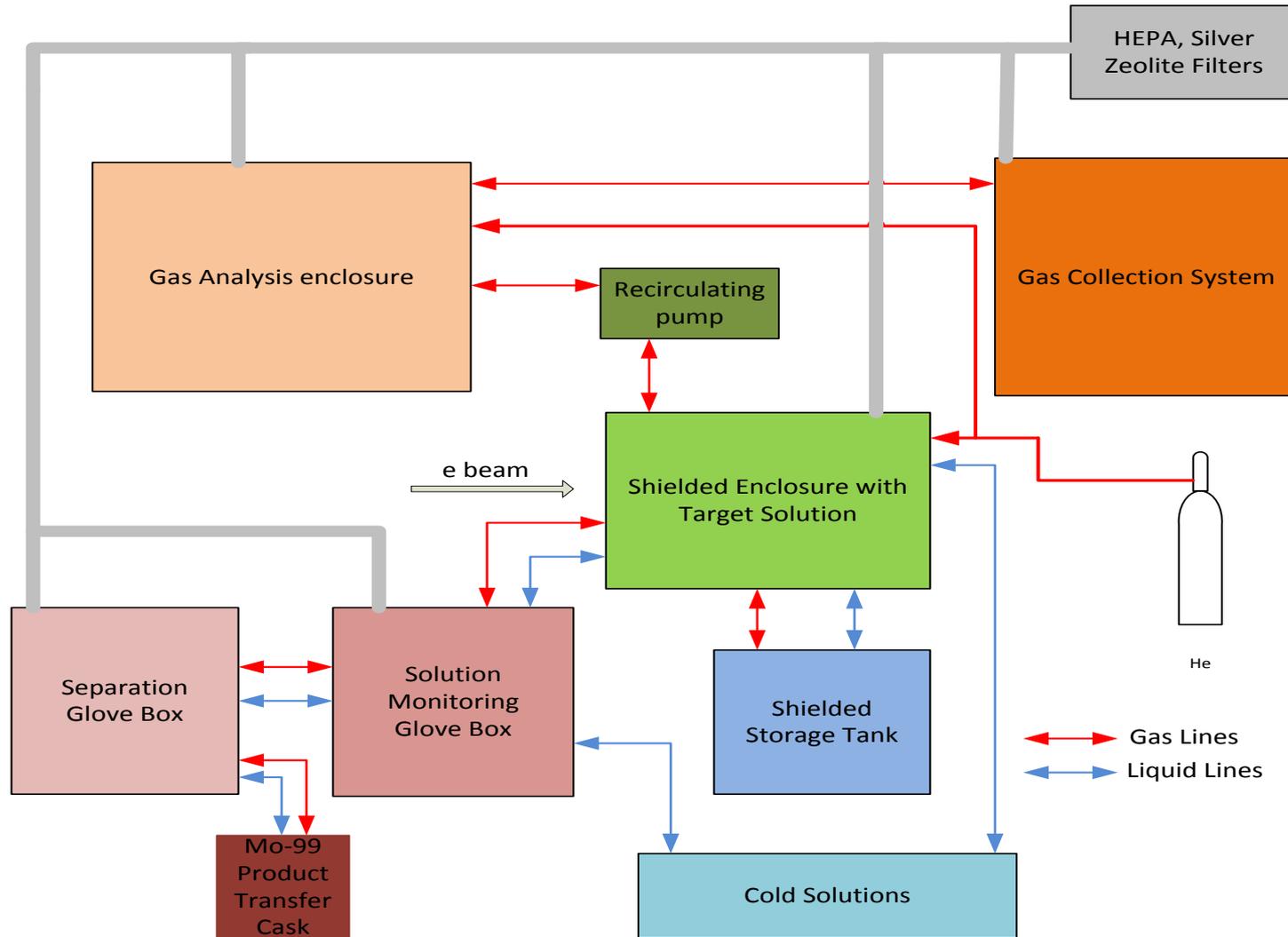
- Linac was initially operated at 18 MeV and now transition to 40 MeV; 10 kW beam power on the target
- 5 L solution will be irradiated with neutrons generated through gamma-n reaction in tantalum target
- The peak power in solution will be  $\leq 0.15$  kW/L.
- Produce up to 2 Ci of  $^{99}\text{Mo}$

## Phase 2

- Linac has being upgraded to 50 MeV maximum energy
  - Experiment will be conducted at 35 MeV beam energy and up to 20 kW beam power
- 20 L solution will be irradiated with neutrons generated in a depleted-uranium (DU) target
- The peak power in solution will be  $\leq 1$  kW/L.
- Produce up to 20 Ci of Mo-99

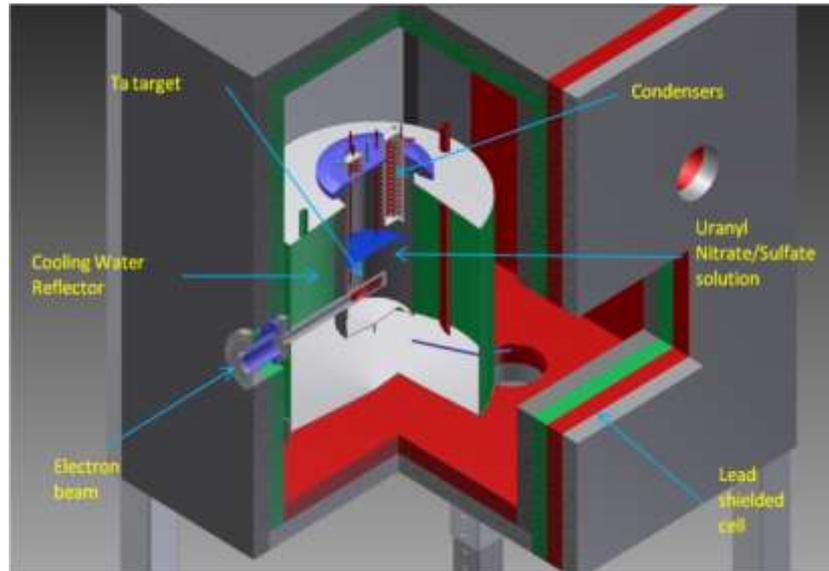


# Mini-SHINE/MIPS experiment (flow diagram)



# 5 L solution irradiation vessel

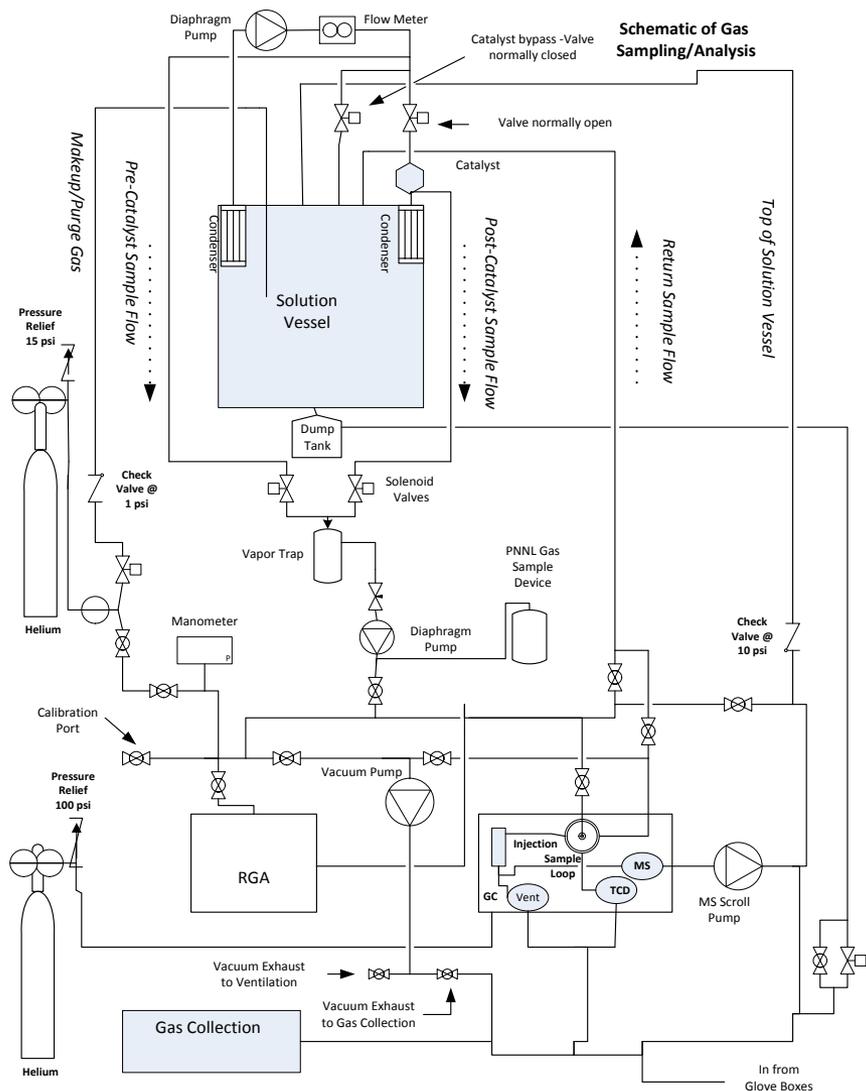
- 5L uranyl nitrate/sulfate solution in a SS 304 vessel
- Large access port for gas analysis, flow loop, thermocouple, neutron- flux monitor, etc.
- 15-cm light-water reflector/cooler



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



# Gas analysis

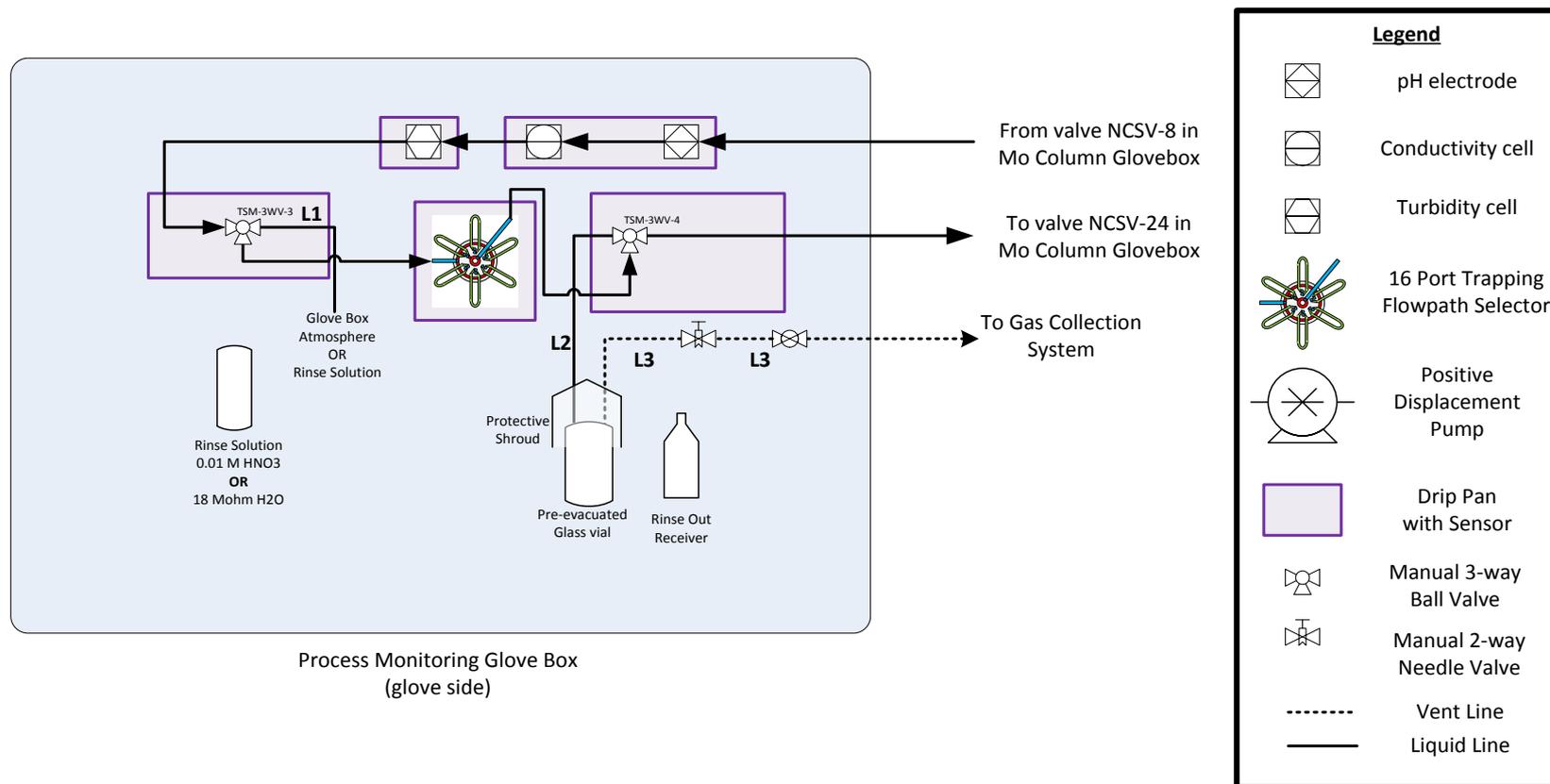


RGA

GC/MS

Gas sampling loop has been tested in the water-irradiation tests

# Sample loop for pH, conductivity measurements, and sample collection



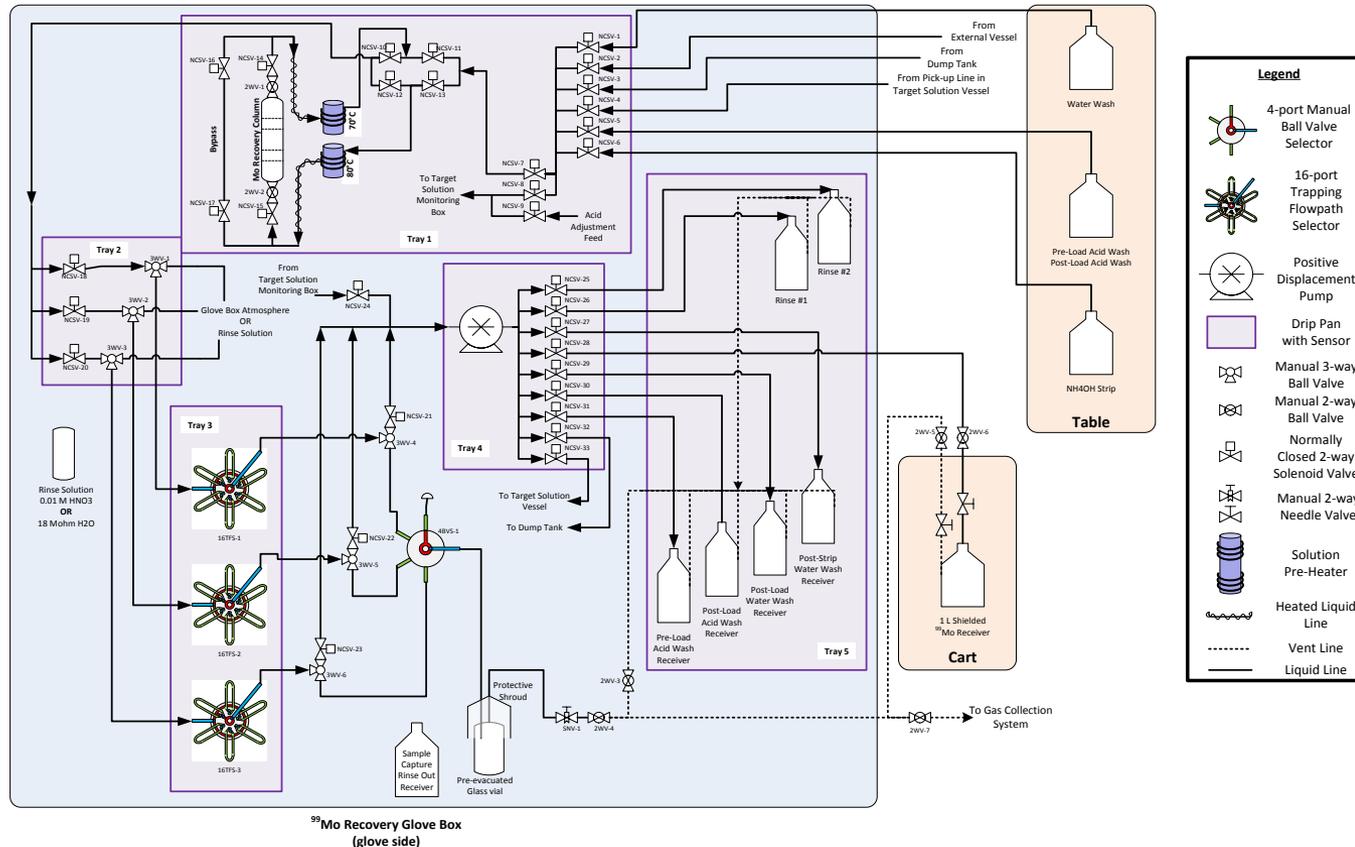
## pH and conductivity meter sample loop

- Continuous operation
- Radiation stability
- Were tested at Van de Graaff facility for radiation stability

## Sample collection system

- The samples range in volume from 1-5 mL
- The samples will be collected without the release of entrained gases into the glovebox atmosphere
- The samples will be collected remotely

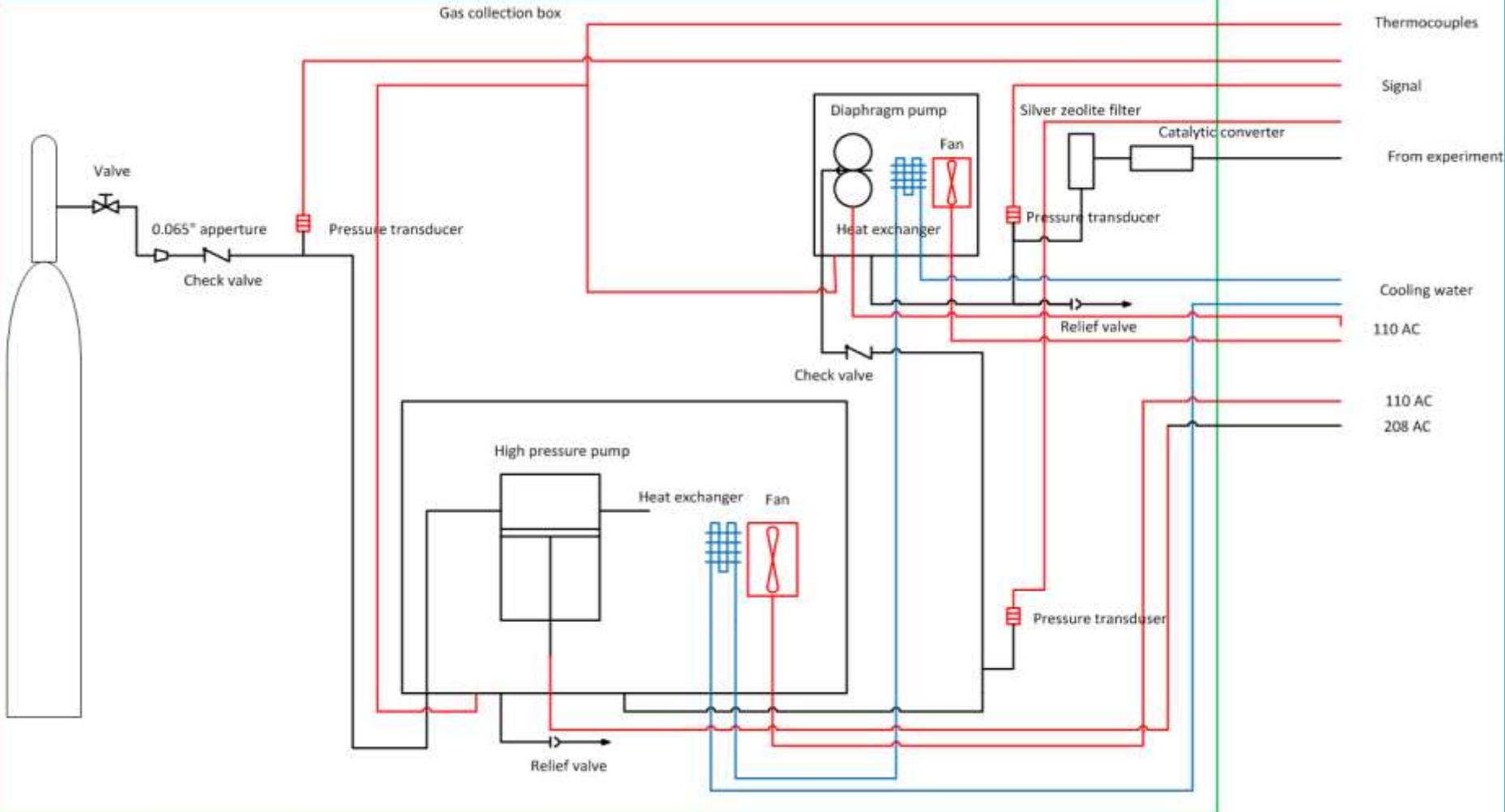
# Separation system design and operations



## Separation system for 5L solution

- 5 L of irradiated uranyl sulfate/nitrate will be passed through the column in the up-flow direction
- Acid wash and water wash will be performed in the up-flow direction
- Stripping of the Mo-99 will be performed in the down-flow direction
- Strip product solution (Mo-99) will be transferred to a lab for purification using the LEU-Modified Cintichem process

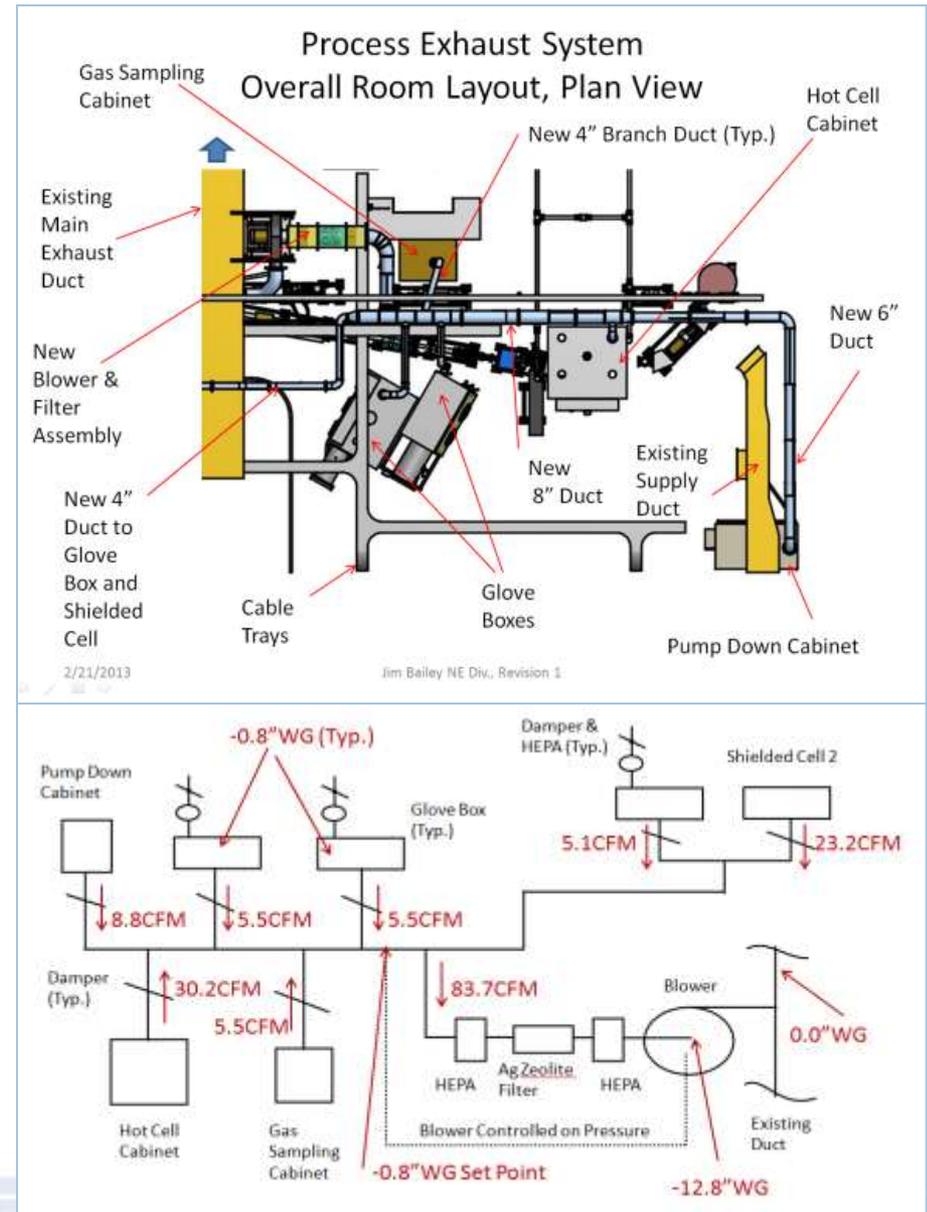
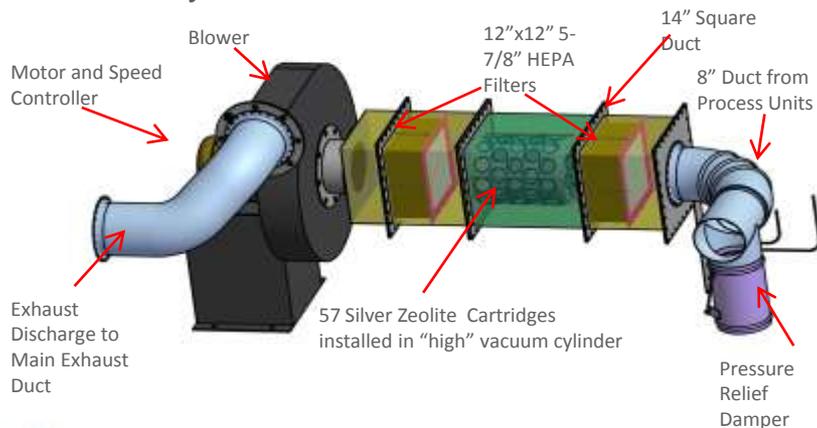
# Gas collection system



Was completely updated after first series of tests. Eliminates possibility for leaks and improves controls and safety

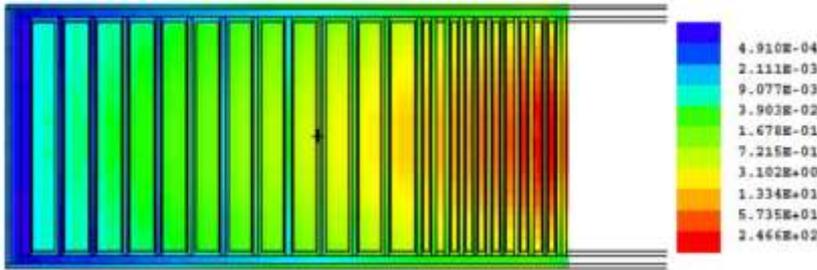
# Process Exhaust System for Gloveboxes and Cabinets

- Maintain glove box pressure between  $-0.5''$  WG and  $-1.5''$  WG per AGS Standards
- Handle flow rate through glove box to be 5 SCFM with HEPA filter at inlet
- Handle leak rate into pump down and sample cabinets to be 5 SCFM each.
- Handle leak rate into hot cell cabinet to be 30 SCFM
- HEPA and Silver Zeolite filters are required at the exhaust from the process exhaust system
- Provide negative pressure relief to avoid damage to system.
- Provide pressure readouts and alarms at each cabinet and across the Blower Filter Assembly.



# Phase 1 and 2 target designs

Phase 2 DU target

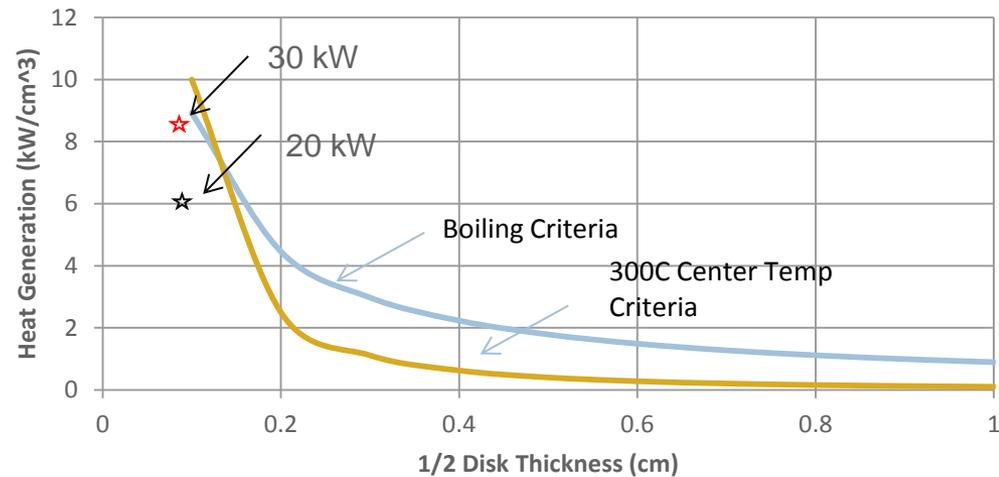


DU disks 2 mm thick  
Target diameter 50 mm  
Water cooling  
Back disks are 6 mm thick

Phase 1 W target

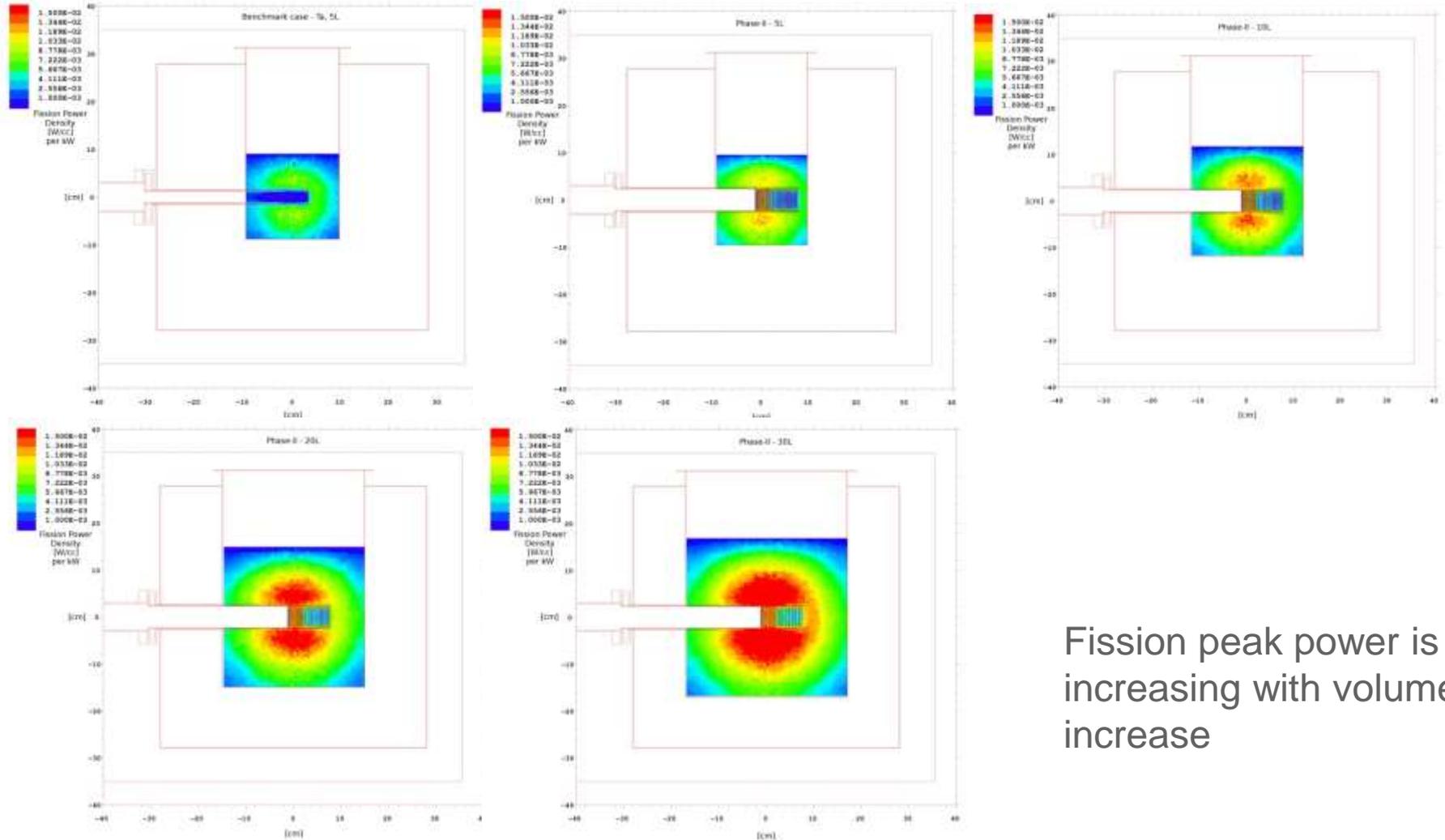


DU Disk Sizing



Parametric plot of heat generation vs. target half thickness for disk target geometry. The red line is defined by 300°C maximum temperature in DU disk; the blue line is defined by 100°C maximum surface temperature to prevent boiling of the coolant.

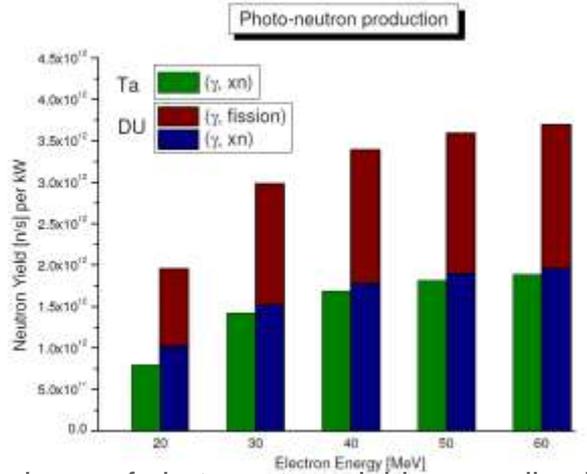
# Fission power distribution for different volumes at 30 MeV electron energy



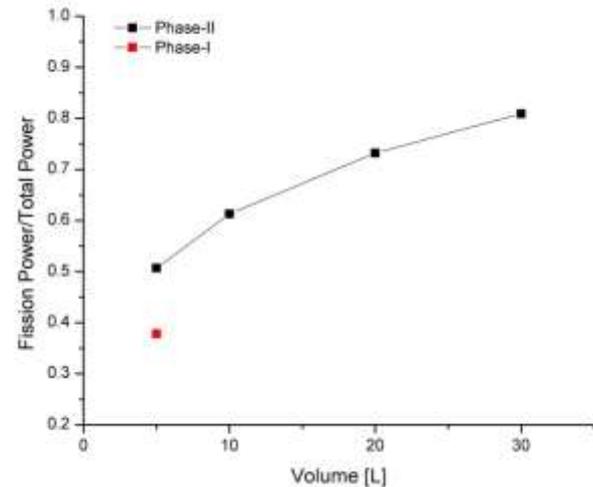
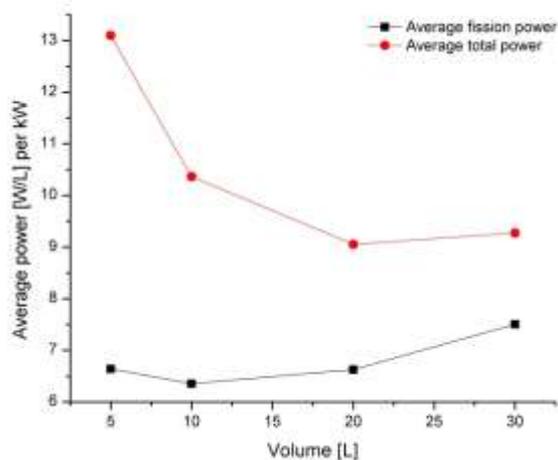
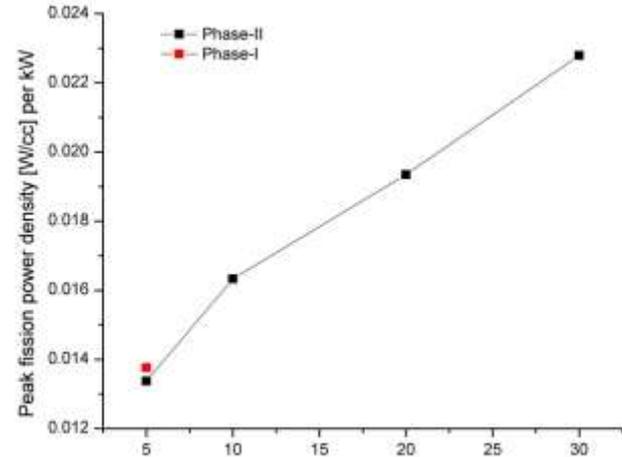
Fission peak power is increasing with volume increase



# Effect of electron energy and volume of the solution on peak fission power



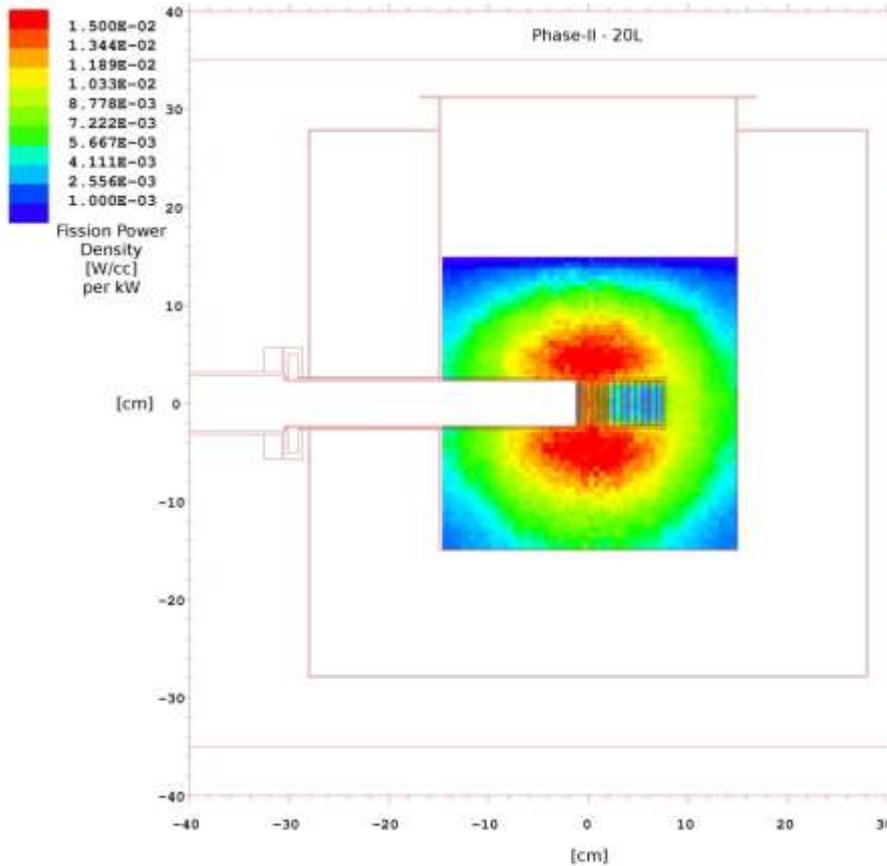
Dependence of photoneutron yields normalized per kW of beam power for Ta and DU targets on electron beam energy simulated with MCNPX



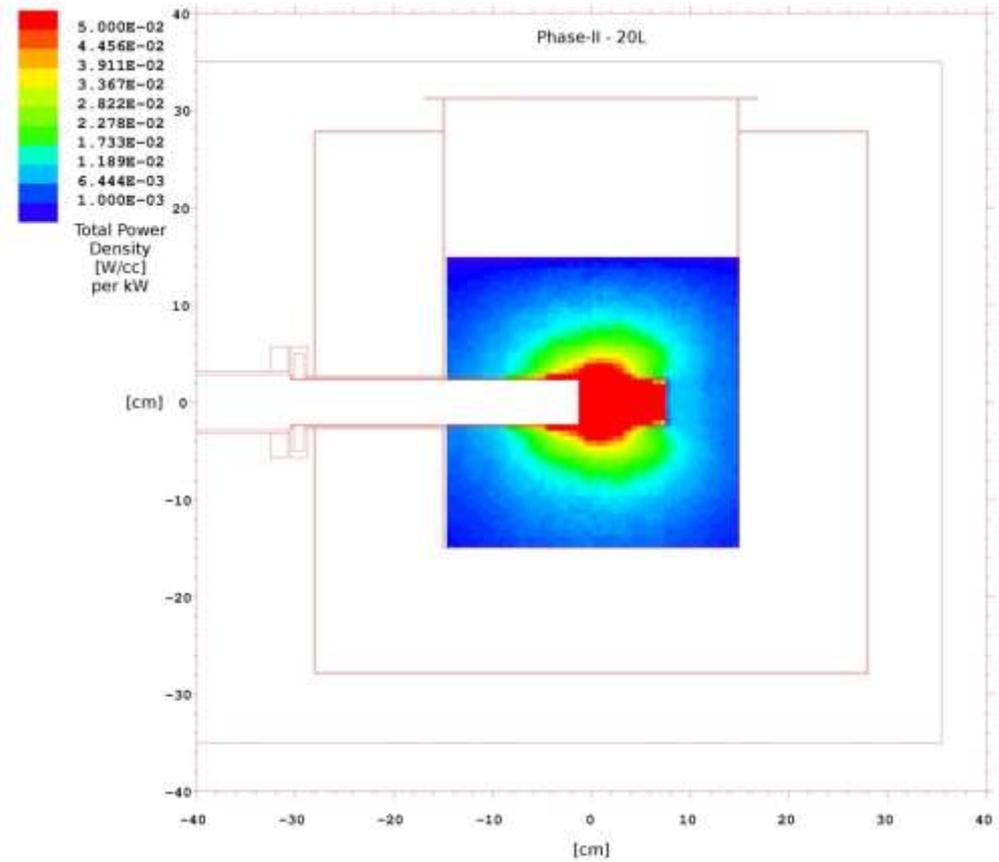
Dependence of the peak and average power in solution at 30 MeV electron energy on volume of the solution



# Phase 2 target solution power deposition



Fission power



Total power



# Concluding Remarks

- Preparation for mini-SHINE/MIPS experiment at the linac facility are underway
- Phase 1 experiments have been started and will continue in April 2013 – June 2013
- Gas evolution rates and pH and conductivity of the solution will be monitored in real time
- Oxidation states of Mo and I partitioning will be evaluated in the samples collected during irradiation
- Multiple concentrations at several powers will be tested
- Samples of Mo-99 can be sent to commercial partner for evaluation
- Preparation for 20 L solution irradiation are under way and irradiation will commence in July-September 2013.

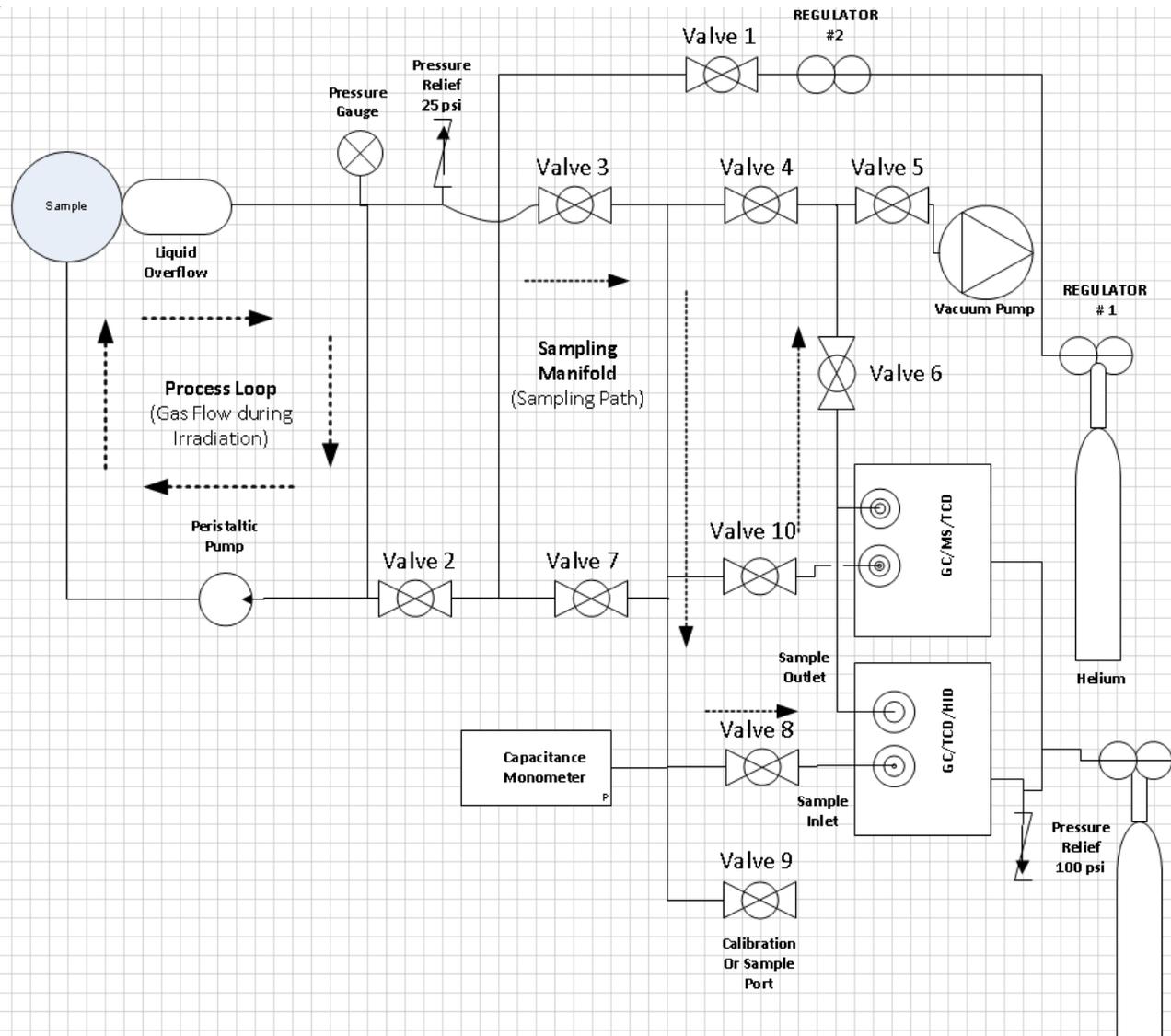
# Acknowledgement

Work supported by the U.S. Department of Energy, National Nuclear Security Administration's (NNSA's) Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC.

# Extra slides



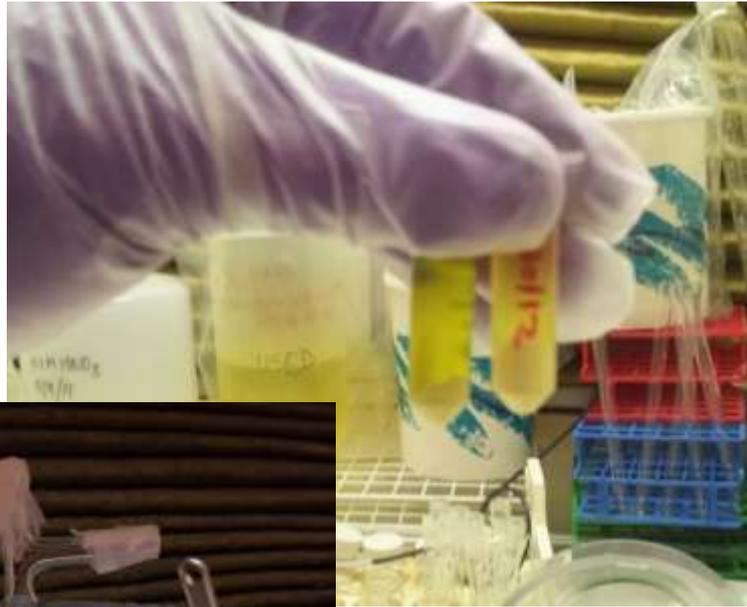
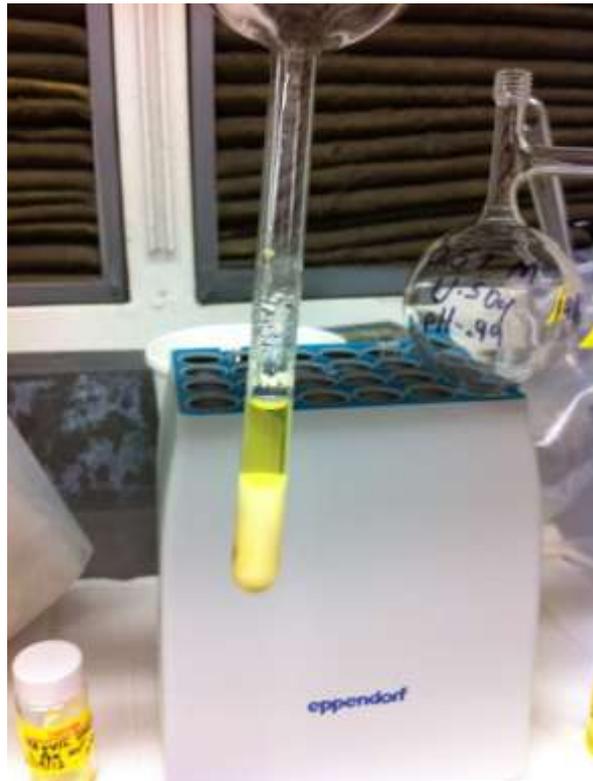
# Measurement of Radiolytic Gas Generation/Corrosion Studies at VDG



# Very Different Radiolysis Behavior for Nitrate and Sulfate Solutions

- Sodium salts
  - Nitrate
    - pH increases with radiolysis
      - Radiolysis of nitrate and reduced-nitrogen compounds requires hydrogen ion for their formation
        - » Appears to proceed all the way to  $\text{NH}_3$
    - $\text{H}_2/\text{O}_2$  ratio  $< 2$  at higher nitrate concentrations
  - Sulfate
    - pH decreases slightly
      - Due to solution concentration from radiolysis of water
    - $\text{H}_2/\text{O}_2$  ratio  $> 2$ 
      - Due to delayed decomposition of hydrogen peroxide to water and  $\text{O}_2$
- Uranyl salts
  - Nitrate
    - pH increases with radiolysis
    - $\text{H}_2/\text{O}_2$  ratio  $< 2$
    - No precipitation of uranyl peroxide
  - Sulfate
    - pH decreases markedly
    - $\text{H}_2/\text{O}_2$  ratio  $> 2$
    - Precipitation of uranyl peroxide

# Precipitation in uranium sulfate samples



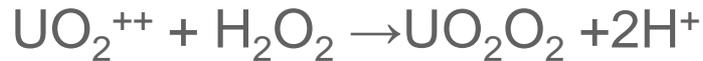
The precipitate dissolved after solution was boiled for a few minutes.

88 g-U/L went to 63.5 g-U/L final pH 0.64 after  $1.712\text{E}+08$  Gy (235 min)

298 g-U/L went to 262 g-U/L final pH 0.58 after  $2.033\text{E}+08$  Gy (270 min)



# Peroxide Formation/Decomposition



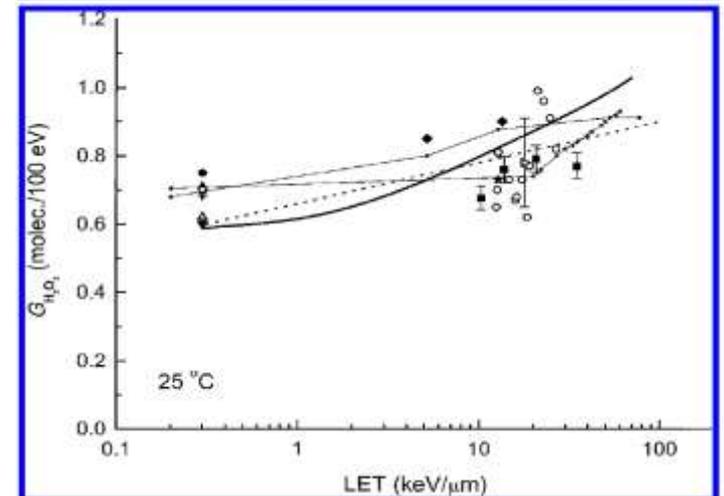
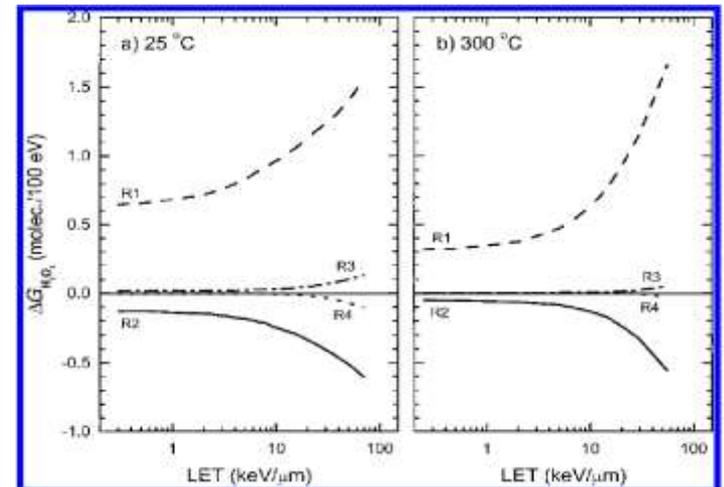
## Thermal decomposition



## Catalytic decomposition by addition of metal salts

Fe, Cu, Ag, Ni, Mn, Ti, I, Cr

- Corrosion studies were postponed to focus on uranyl peroxide precipitation



LET dependent peroxide formation

Jintana Meesungnoen, Jean-Paul Jay-Gerin, Abdelali Filali-Mouhim, and Samlee

Mankhetkorn, Can. J. Chem. Vol 80, 2002 p 68

# Addition of Ferrous Sulfate eliminated Precipitation

Additive	Energy Deposited	Initial [UO <sub>2</sub> (SO <sub>4</sub> )]	Final UO <sub>2</sub> (SO <sub>4</sub> )	pH	pH	H <sub>2</sub> μmoles	O <sub>2</sub> μmoles	G -Value	G -Value	H <sub>2</sub> to O <sub>2</sub>
	(Gy)	[g-U/L]	[g-U/L]	Initial	Final	Total Produced	Total Produced	H <sub>2</sub> /100eV	O <sub>2</sub> /100eV	Ratio
9.94 mg/L FeSO <sub>4</sub>	2.31E+08	123.5	No Precipitation	1.42	1.44	540	343	0.011	0.007	1.57
99.4 mg/L FeSO <sub>4</sub>	2.20E+08	123.5	No Precipitation	1.42	1.37	462	302	0.010	0.006	1.53
Zr metal	2.32E+08	298	260	1.0	0.67	1112	460	0.023	0.010	2.42

- Addition of ferrous sulfate eliminated precipitation of uranyl peroxide
  - Note negligible pH changes and H<sub>2</sub>/O<sub>2</sub> mole ratios of under 2
- Chips of Zr metal did nothing to destroy peroxide
  - Note significant decrease in pH due to precipitation of uranyl peroxide
  - Note the high H<sub>2</sub>/O<sub>2</sub> mole ratio
- We don't want precipitation inside the mini-SHINE any more than SHINE wants it in the Target Solution Vessel so we will use a micro-SHINE setup to look for precipitation during water irradiation/testing

